Improved Second Harmonic Generation from Organic-Dye-Doped Polymer/Silica Hybrid Materials

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In this study, we investigated the second-order optical nonlinearity and its thermal stability of DR1 (disperse red 1) doped poly(methyl methacrylate) (PMMA)/silica gel films. We found that in situ polymerization of sol−gel precursors (tetraethoxysilane, TEOS) in a polymer generated a hybrid matrix which is a good tradeoff between a silica gel and a polymer matrix. The nonlinear thermal stability of the hybrid system increased significantly compared to that of a poled DR1/PMMA film. Our result proved that the combination of a poled polymer and the sol−gel technique provides a way to increase the thermal stability of nonlinear optical thin films fabricated from existing materials rather than synthesizing new chemical compounds. Several factors which affect the second-order optical nonlinearity of the hybrid system were also examined.

Introduction

The two most popularly used matrixes in the study of optical second-order nonlinearity are polymer[1] (e.g. poly(methyl methacrylate) (PMMA)) and silica gel.[2] The low glass transition temperature (T_g) of PMMA prohibits its application as a photonic device (e.g., a nonlinear optical waveguide). Though high T_g polymers (like polyimide) are potentially an applicable host, progress on doped high T_g materials requires the engineering of nonlinear dyes which are able to consistently withstand the higher softening temperature of the host matrix without decomposing, thus imposing an additional load to the material requirements. On the other hand, silica gel prepared by the sol−gel technique is fragile, and it is not easy to obtain low transmission loss optical waveguides when organic dyes are doped,[3] because the optical losses of films fabricated by the sol−gel technique depend sensitively on annealing temperatures. For organic nonlinear optical (NLO) dye-doped materials, annealing temperatures can hardly exceed 200 °C, which is too low to obtain a homogeneous small pore size silica gel matrix. Organic/inorganic hybrid or organic modified silicate (ORMOSIL) combines the advantages of the flexibility of a polymer and the rigidity of silica.[4] Sol−gel provides the unique technique to prepare a hybrid organic/inorganic composition, because of the nature of the wet chemical reaction. In situ polymerization of sol−gel precursors (e.g., tetraethoxysilane(TEOS)) in a polymer (e.g., PMMA) reduces the brittleness of pure inorganic glasses, which could help prevent stress cracking during the curing process. The silica on the contrary acts as a reinforcing agent, imparting increased hardness, compressive strength, heat distortion temperature, and plateau modulus and lower thermal expansion coefficient to the polymer.[5] The second-order optical nonlinearity of dye-doped polymer/silica gel hybrid materials was also studied,[6] though not systematically.

The motivation of the current work is to explore the second-order nonlinearity of dye-doped hybrid polymer/silica gel films. By mixing polymer/silica gel in various molar ratios, an increase of the glass transition temperature T_g is expected with an increase of the silica gel molar ratio. As it has been known that there are chemical bonds between PMMA and hydroxylated silica at low pH,[8] and silica gel is much more rigid than

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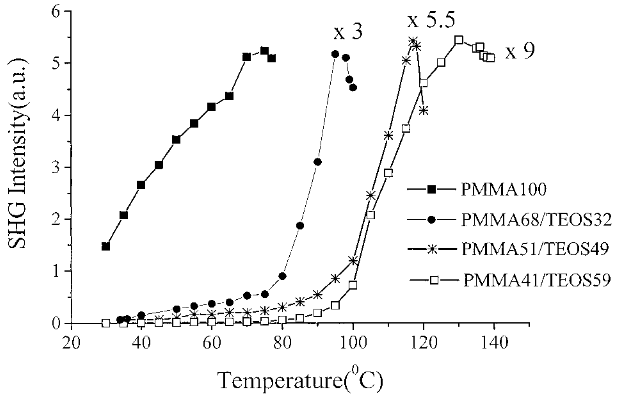

Figure 1. Changes of SHG intensity versus poling temperature for various molar ratios of TEOS incorporation into the PMMA matrix. Note the multiplication factor for each curve.

PMMA, the interleaving of the silica long chain into the PMMA should prohibit the movement of PMMA, thus providing a hybrid matrix which should have better thermal stability than pure PMMA. The increment of T_g is very interesting. First, we expect a dramatic improvement of the nonlinear thermal stability of the hybrid system due to the rising T_g, and second, materials of different T_g have various kinds of potential applications, such as creating an inversion type waveguide structure for efficient frequency doubling.[7]

In this study, we investigated extensively the second-order nonlinearity and its thermostability of an organic-dye-doped polymer/silica hybrid NLO material. The main purpose of the work is to find the quantitive relationship between the nonlinear thermal stability of the hybrid system and the molar ratio of the incorporated silica gel.

Experimental Section

We selected an organic dye, DR1 (disperse red 1), as the NLO dopant, because its nonlinearity has been clearly revealed. Different quantities of sol−gel precursors (TEOS, water, and acid) were added to PMMA/THF solution. The H_2O/TEOS molar ratio (so-called R value) was kept at 4. We labeled our samples as PMMAx/TEOSy. The number after PMMA denotes the molar percentage of MMA; the number after TEOS denotes the molar percentage of TEOS. DR1 was then added to the solutions. A homogeneous uniphase solution was obtained. Clean glass slides coated with indium−tin oxide (ITO) on one side were used as substrates. A thin film on an ITO plate was dipped under a carefully controlled environment (humidity and temperature). The thickness of the films was between 1 and 1.5 μm. Optically clear thin films of various polymer/silica molar ratios were dipped. The films were corona poled at elevated temperatures. The poling voltage was around 5 kV; the poling current was about 1 μA. In situ transmitted second harmonic generation (SHG) measurement was carried out to investigate the nonlinearity of the thin films under poling.[9] The NLO thermal stabilities of the poled films were studied by measuring the SHG relaxations when the poled films were heated again. The DR1-doped pure PMMA film was also fabricated in comparison.

Results and Discussion

Thermal Stability. Figure 1 shows, for different molar ratios of TEOS incorporation, the changes of SHG intensity with temperature under poling. Generally, SHG intensities increased with increasing temperature. After a maximum was reached, the intensity began to drop. For a pure polymer matrix, it was clear that the drop of SHG was due to the rapid increase of the conductivity of the film near or above its glass transition temperature T_g.[10] So the drop point was closely related to the T_g of the film. We can clearly see from the figure that the temperature at which the SHG began to drop significantly increased when a larger amount of TEOS was incorporated. The increase of T_g can be simply explained as the result of more intense interaction between silica and PMMA. Higher molar ratio of TEOS will generate longer silica chains and a more complete network. Consequently, the mobility of PMMA was prohibited.

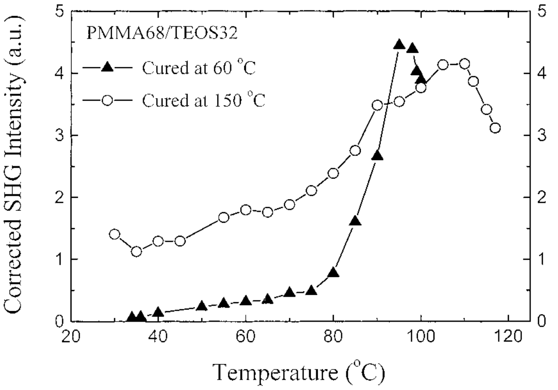

Figure 2. In situ SHG intensity with respect to temperature during poling. The matrix composition is PMMA68/TEOS32. Two cases were studied. The first sample was prebaked at 60 °C for 1 h; the second sample was prebaked at 150 °C for 15 h.

The dependence of T_g on curing history was also observed. A higher curing temperature will result in more complete gelation, and generate a denser and more compact silica gel. Consequently, the interaction between PMMA and silica gel will be stronger. All these contribute to a more rigid hybrid matrix and a higher T_g. Our experimental result is shown in Figure 2. Two curves are shown in Figure 2. In the first case, the film was precured at 60 °C for 1 h before poling, while in the second case, the film was precured at 150 °C for 15 h. As expected, the temperature at which the SHG intensity began to drop increased from 97 °C (60 °C precured) to 115 °C (150 °C precured).

Another evidence of a T_g change can be obtained by measuring the thermal stability of the film. After the poling temperature reached the drop point of SHG, we stopped heating and let the temperature go down slowly at the rate of about 1 °C/min; the poling field was not moved away until room temperature was reached. Then the film was heated again to high temperature without poling, and the relaxation of SHG intensity was recorded. Figure 3 shows the experimental results. Similar to that of the poling process shown in Figure 1, a large amount of TEOS incorporation retarded the SHG relaxation temperature. We define the temperature T_{ref} as the temperature at which SHG relaxes to its half-maximum. Compared with a pure PMMA matrix, T_{ref}

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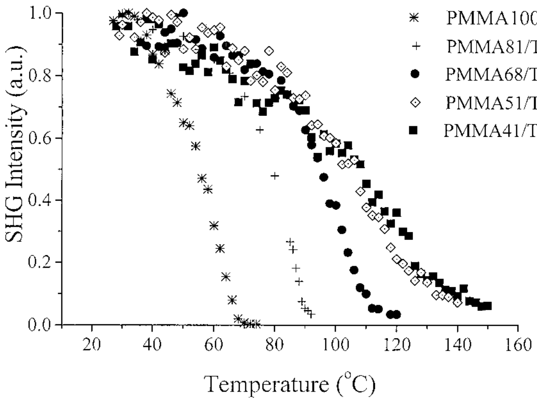

Figure 3. Relaxation of SHG intensity versus annealing temperature for various molar ratios of TEOS incorporation into the PMMA matrix.

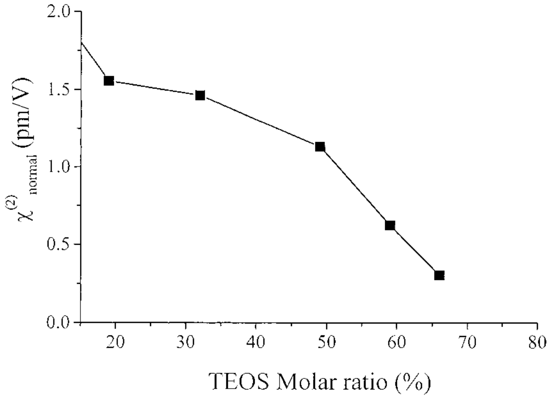

Figure 4. Normalized $\chi^{(2)}$ versus the molar ratio of incorporated TEOS.

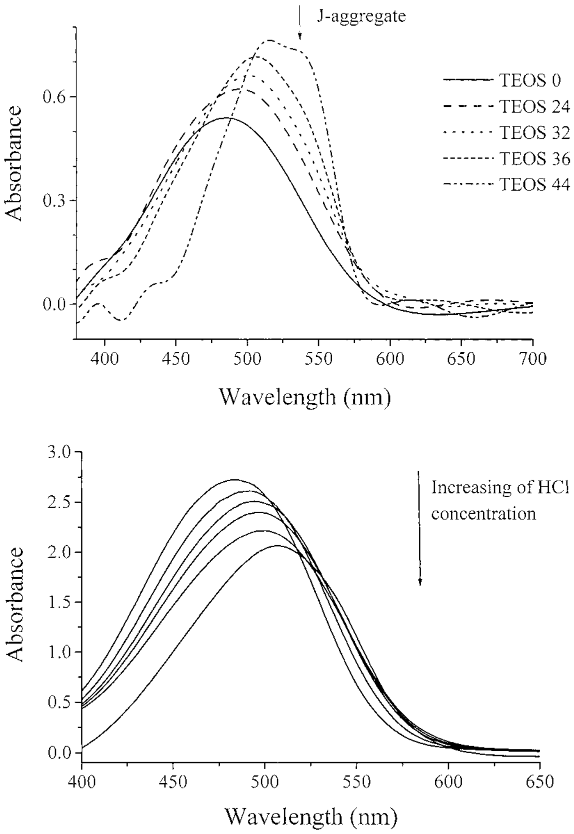

Figure 5. (a, top) Absorption spectra of DR1-doped PMMA/TEOS hybrid composites. The red shift of the absorption peak indicates DR1 protonation. (b, bottom) Absorption spectra of DR1-doped PMMA when acid water was added.

rose from 57 to about 120 °C for a composition of 36 mol % TEOS incorporation. Saturation of T_{ref} was obvious when a large amount of TEOS (more than 50 mol % of TEOS) was added. We thought that the saturation mainly came from the limited poling temperatures we used. To avoid molecular degradation, we never used a poling temperature higher than 150 °C for a poling time of 1 h. We believe that when a large amount of TEOS is incorporated, a much higher temperature or a much longer time is necessary to complete the hydrolysis and condensation process.

Strength of Nonlinearity. Though a larger amount of TEOS incorporation will increase the T_g of the matrix, it also reduced the SHG intensity of the film. Figure 4 plots the changes of normalized $\chi^{(2)}$ versus incorporated TEOS molar ratio. Since the thickness of the film and the concentration of DR1 molecules inside the film were different for different amounts of TEOS incorporation, correction is needed so that the normalized $\chi^{(2)}$ only reflects the changes of matrixes. Normalization was done in the following way:

$$\chi^{(2)}_{\text{normal}} = \chi^{(2)}/A$$

where $\chi^{(2)}_{\text{normal}}$ and $\chi^{(2)}$ are the corrected and measured values, respectively, and A is the absorbance of the film. Here we have supposed that, for all the compositions, the DR1 molecule had the same transition possibility. We can see clearly from Figure 4 that $\chi^{(2)}_{\text{normal}}$ decreased monotonically with increasing TEOS molar ratio. There are several possibilities for the cause of the decrease: (i) interactions of sol–gel precursors with DR1. These include DR1 protonation due to the existence of H^+ and interaction of DR1 with hydrolyzed TEOS. Both of the factors reduce the hyperpolarizability of the molecule, so that the nonlinearity of the film declines. (ii) If the hybrid composite turns from thermal-plastic to thermal-set when TEOS is added, trapped DR1 molecules in a hybrid matrix will lose the ability to orient along the direction of the external poling field. As we can see from Figure 1, the SHG intensity rose only when the conductivity of the film became sufficiently low. At that moment, however, it may already be too late to orient the molecules since the matrix had been stuck.

To find the main causes of the reduction of nonlinearity, extensive works were done to distinguish the factors such as protonation, interaction, and thermal-set behavior.

First, absorption spectra of films in the visible before and after poling were examined. A continuous red shift of the absorption maximum can be clearly seen when a larger amount of TEOS (HCl as well) was incorporated (see Figure 5). The red shift of DR1 in acid environment indicated protonation. However, after poling, the absorption maximum turned back; thus, the absorption profiles were very similar to that of DR1 in pure PMMA matrix. We also measured the SHG of DR1-doped PMMA when HCl was added. We saw an obvious red shift of the absorption peak as well. In this case, however, the SHG intensity of the films did not decrease. Therefore, we can rule out the possibility that protonation of DR1 caused the decrease of the SHG intensity in the hybrid composite.

Second, we examined again the results shown in Figure 2. We recall that we prepared two samples of PMMA68/TEOS32 composition. One sample was prebaked at 60 °C for 1 h; the other was prebaked at 150 °C for 15 h. If the hybrid material turns thermal-set after complete hydrolysis and condensation, we would not be able to align NLO molecules; thus, we would expect much smaller SHG intensity when we heat the sample at higher temperature and for a long enough time. We have mentioned that after prebaking at 150 °C for 15 h, the appearance of the SHG maximum was retarded compared to the case of prebaking at lower temperature. However, the two samples showed approximately the same maximum of SHG intensity. The result strongly implies that, at the composition of PMMA68/TEOS32, the hybrid material is still thermal-plastic rather than thermal-set. Doped molecules should still be able to orient along the external poling field. Therefore, we are quite confident that interaction between hydrolyzed TEOS with DR1 is the main cause of decreasing SHG intensity.

Conclusion

Our experimental results show that incorporation of silica gel into PMMA can significantly improve the thermal stability of the system. It must be noted that the improvement strongly depends on what kind of polymer is used as the basic matrix. When 10% of DR1 was doped into PMMA in our case, the T_g of the material was only around 60 °C as determined from differential scanning calorimetry (DSC) measurement. Therefore, though the improvement of thermal stability was obvious, the final T_g was not high, even when compared with some sorts of polymers including polyimide and graft PMMA where a chromophore is tethered to the polymer backbone. However, what we provided in this paper is a technique which should be useful for further consideration of preparing a hybrid composite of better thermal stability from existing materials instead of synthesizing new chemical compounds. On the other hand, the controllable T_g will be interesting to material scientists and will have potential utility in fabricating new photonic materials and devices.

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