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Thermal stability of ZrO_2 nanoparticle-polymer composite volume gratings incorporating multifunctional chain transfer agents

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We have recently demonstrated the enhancement of the saturated refractive index modulation (Δn_{sat}) of ZrO_2 nanoparticle-polymer composite (NPC) volume gratings recorded at short grating spacing by doping chain transferring a single functional thiol (mono-thiol) as a chain transfer agent (CTA) [1]. We have also achieved substantive shrinkage suppression in this NPC system. Since crosslinking networks can be controlled by introducing multifunctional thiols in photopolymers [2], it is expected that another important property of recorded NPC volume gratings, the thermal stability, may also be improved. Here we report on a thermal stability analysis of ZrO_2 NPC volume gratings containing thiols with varied functionalities.

We employed three types of thiols as CTAs, mono-, di- and tri-thiols with single, two and three functionalities [3], respectively. They were doped, together with titanocene as a radical photoinitiator, in acrylate monomer, 2-propenoic acid, (octahydro-4,7-methano-1H-indene-2,5-diyl)bis(methylene) ester [1,3]. Surface-modified ZrO_2 nanoparticles (the average core size of 3 nm) of 35% [4] were dispersed in the above monomer syrup. This mixture was cast on a 50-µm-spacer loaded glass plate and was covered with another glass plate after drying for film samples. Plane-wave NPC volume gratings of 1-µm spacing were recorded in film samples at a wavelength of 532 nm and at a recording intensity of 50 mW/cm^2.

We employed a holographic technique for our thermal stability measurement by which the percent thermal expansions and linear coefficients of thermal expansion (CTEs) could be estimated for ZrO_2 NPC volume gratings containing thiols with varied functionalities. A detailed measurement technique is described in [5]. Figure 1(a)-1(c) shows a temperature dependence of percent thermal expansion relative to the value for thickness of recorded film samples with varied concentrations of thiols at 25 °C. It can be clearly seen that thicknesses of the film samples linearly increase with increasing thiol concentrations for each scenario. This is caused by a reduction in the average polymer chain length by incorporating chain-transferring thiols [3]. It can be also seen that an increase in thiol functionality results in a decrease in percent thermal expansion, since the polymer chain length increases with increasing thiol functionality, showing the improvement of thermal stability by doing multifunctional thiols. Figure 1(d) illustrates CTEs as a function of thiol concntration for film samples doped with mono-, di, and tri-thiols. It can be seen that an increase in thiol functionality results in a decrease in CTE. This result implies that higher crosslinking network can be produced

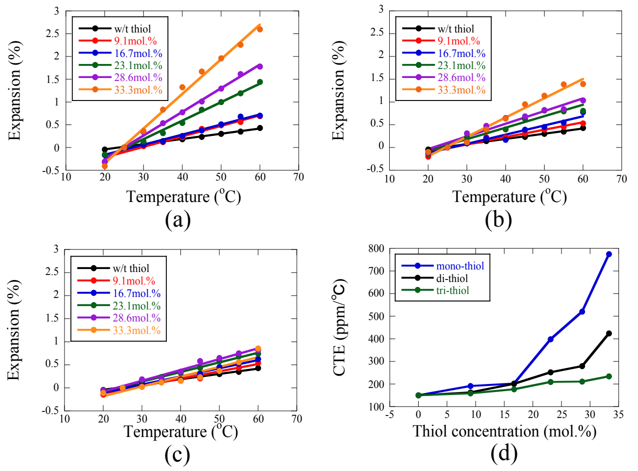

Fig. 1. Temperature dependences of thermal expansion for film samples doped with (a) mono-, (b) di-, and (c) tri-thiols of various concentrations, where solid lines denote the least-squared linear fits to the data. (d) Thiol concentration dependence of CTE for film samples doped with mono-, di-, and tri-thiols. Solid lines are a guide to the eye.

with increasing thiol functionalities. For example, the tri-thiol doped film sample provides a significant reduction in CTE as large as 80% as compared with the mono-thiol doped one.

In conclusion, we have studied thermal stabilty of ZrO_2 NPC volume gratings containing thiols with varied functionalities. We have found that the use of tri-thiol as a CTA shows good performance in thermal stability as well as the high spatial frequency response [3] for the use of thiol-doped NPC volume gratings in holography and neutron optics [1]. Our results presented in this paper would offer a method of improving NPC volume gratings by chemeical modifications.

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