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High performance holographic gratings formed with novel photopolymer films containing hyper-branched silsesquioxane

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Dedicated to Professor Teiji Tsuruta on the occasion of his 88th birthday (Beiju).

Abstract

A transparent photopolymer film was prepared by embedding the epoxy cured octaaminophenylsilsesquioxane (hyper-branched POSS) into poly(vinyl chloride) (PVC) matrix containing vinyl monomers. Holographic gratings were successfully generated in that films by irradiation of laser light with 532 nm wavelength.

The diffraction efficiency was increased with increasing the hyper-branched POSS concentration up to 15 wt%. DSC and TG analysis indicated the plasticizing effect of POSS in photopolymer that loosened the polymer matrix. This plasticizing effect made the monomer diffusion much more effective providing higher diffraction efficiency (D.E. ~ 80%) compared to the film without hyper-branched POSS (D.E. ~ 50%). The diffraction efficiency started to decrease with further higher concentration of POSS, because the polymer film became less transparent.

Low volume shrinkage of 1.64% could be also obtained in recording of slanted holographic gratings.

Keywords: Hyper-branched POSS; PVC; Photopolymer film; Holographic gratings; Volume shrinkage

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1. Introduction

Photopolymers have been considered as recording materials for holographic data storage and display application [1–4] for several decades [1,5] because of their inherent advantage of one step processing, no post treatment, large dynamic range, good optical quality and high flexible formulation over inorganic systems [6,7].

For the fabrication of holographic gratings, photopolymer systems consist of polymer matrix, photo-reactive monomer such as vinyl, typically acrylic monomers, cross-linking agent, photo-initiator, and photo-sensitizer [8,9] etc. In this system, photo-initiator absorbs the incident light and produces active radicals that initiate the monomers to polymerize. When the monomers start to be

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polymerized in the bright region, a concentration gradient is created between bright and dark regions. This difference in concentration induces monomer diffusion from the dark to bright region. The refractive index modulation is arisen from the compositional difference of the molecular chain in the adjacent two regions [10–12] mainly governed by the diffusion of photo-reactive monomers.

However, in some case, photo-reactive monomers can not diffuse easily through the hard polymer matrix. This problem can be solved by adding the plasticizer in photopolymer formulation which induces the softening of polymer matrix [10,13]. Kim et al. [14] reported that carbon base dendrimer molecules could provide large free channels for monomer diffusion due to their inherent voids. The intramolecular spaces or branching of dendrimer also loosens the polymer matrix.

Recently, many research groups have proposed the different composition of photopolymer using organic or organically modified inorganic nano-particle [5,15,16] to improve the holographic performance such as high degree of photosensitivity, dimensional stability and refractive index modulation. The main obstacle of using nano-particle is the large scattering resulting from the aggregation of nano-particles and low photosensitivity, which were substantially improved by introducing the organically modified nano-particles [17].

In this research we focused on the novel recording materials by introducing the epoxy cured silsesquioxane (hyper-branched POSS) molecules in PVC matrix. The incorporation of silicone based hyper-branched POSS should increase the free volume in matrix and act as plasticizer, and in addition, provide incompatibility with carbon based monomers, which should enhance the diffusion process of photo-reactive monomers during grating formation. Prior to making photopolymer films, octaaminophenylsilsesquioxane (OAPhPOSS) was synthesized and cured with neopentylglycol diglycidylether giving a partial cured hyper-branched POSS. The hyper-branched POSS eradicated the aggregation of OAPhPOSS, resulting in a very transparent photopolymer film and also removed the brittleness of the PVC matrix that might assist the diffusion of monomers.

The dynamic real-time diffraction efficiency and degree of volume shrinkage of photopolymer films with and without hyper-branched POSS were investigated by real-time monitoring and asymmetric grating formation, respectively.

2. Experimental

2.1. Materials for holographic recording

PVC (M_w 43,000) (Aldrich) was used as polymer matrix without any purification. Tri(propylene glycol) diacrylate (TPGDA) (Aldrich) and *N*-vinylpyrrolidone (NVP) (TCI) were used as photoreactive monomers. Diphenyliodonium hexafluorophosphate (Alfa Aesar, 98%), 3,3′-carbonylbis(7-diethylaminocoumarin) (Acros, 99%) were used without purification as photoinitiator (PI) and photosensitizer (PS), respectively. Hyper-branched POSS was prepared by curing the synthesized octaaminophenylsilsesquioxane (OAPhPOSS) and neopentylglycoldiglycidylether (NPGDE) (Aldrich) as following description.

2.1.1. Synthesis of octaphenylsilsesquioxane

Octaphenylsilsesquioxane was synthesized according to Ref. [18]. For the synthesis, 75 mmol of phenyltrimethoxysilane and 112.5 mmol of deionized water were taken in 75 ml of benzene in 200 ml round bottom flask. To the solution, 6 mol% of benzyltrimethylammoniumhydroxide (BTMAOH, 40% w/w in methane) on the basis of trimethoxysilane was added and stirred at reflux temperature for 4 h in nitrogen atmosphere. The precipitation formed was collected by filtration, washed with methanol and hexane. The washed sample was recrystallized from dichloromethane/acetone and dried in vacuum at room temperature for 12 h. ^{1}H NMR ($CDCl_3$, ppm): 7.75 (dd, $J_1 = 7.5$, $J_2 = 1.0$ Hz, *o*-H), 7.42–7.47 (tt, $J_1 = 7.5$, $J_2 = 1.0$ Hz, *p*-H), 7.36 (t, $J = 7.5$ Hz, *m*-H); MALDI-TOF MS: 1055.10 ($M^+ + Na^+$), ^{29}Si NMR (ppm): −78.3.

2.1.2. Synthesis of octanitrophenylsilsesquioxane [19]

Fuming nitric acid, 52 ml (94%) was added to a 200 ml of flask and cooled to 0 °C by ice bath. Then 8.55 g (8.28 mmol) of octaphenylsilsesquioxane was added slowly in small portions with vigorous stirring. After addition was completed, the solution was stirred at 0 °C for 30 min and further stirred at room temperature for another 20 h. The solution was filtrated with glass wool and precipitated by pouring the solution onto 250 g ice. A very faintly yellow precipitate was collected, washed several time with water and ethanol, and vacuum dried at 70 °C for 10 h (yield 10.12 g, 7.27 mmol, 87%).