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Diffraction Behaviors of New Photopolymers Containing the Dendritic Molecule

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Abstract: Photopolymers are attractive materials for holographic 3-D data storage because of their high photosensitivity and large refractive index modulation. We synthesized the six-armed dendrimer for fabricating the new photopolymer. It was prepared using the initiating mixture of hexaarylbiimidazole (HABI), mercapto-benzoxazole (MOBZ), and 2,6-bis(4-diethylaminobenzylidene)cyclopentanone (DEAW), which is sensitive to 514 nm wavelength. The holographic gratings were fabricated successfully in these photopolymer samples by conventional optical interference method. We investigated the effect of dendrimer, either as a binder or as a plasticizer in the cellulose acetate butyrate (CAB), on the diffraction behavior. The addition of only 1 wt% of dendrimer-I into the CAB significantly increased the diffraction efficiency. The sample doped with dendrimer showed around 80-83% of the diffraction efficiency.

Keywords: photopolymer, dendrimer, holographic grating, diffraction efficiency.

Introduction

Photopolymer (PP) systems have attracted much attention in recent years since they proved to be promising materials systems for holographic 3-D data storage and display applications.[1-5] Holographic gratings can be efficiently fabricated in the photopolymer films by laser-optical interference methods. Therefore, new photopolymer systems were developed due to the advantages of dry process, ease of storing information, good light sensitivity, large dynamic range, good optical quality, and relatively low cost.[5,6]

A number of photopolymerizable material systems for holographic applications have been developed in the past.[7,8] The storage medium should have low absorption at the writing beam wavelength to achieve uniform recording through the thickness of the material and exhibit small light scattering to minimize the noise-to-signal ratio in recording images. There is a large portion of mobile species for the holographic writing process. They must undergo rapid and a high degree of photoinduced polymerization followed by monomer diffusion. Generally, the photopolymer typically consists of polymer binders, vinyl or acrylic monomers, photoinitiator system, plasticizer, crosslinker, and sensitizing dye.[9-11] The host polymer binder acts as a supporting rigid matrix containing the other low molar mass components. The monomers serve as another main species to control the index modulation induced by optical interference.

The basic principle how to elaborate gratings in photopolymer films had been well reported previously.[12,13] First of all, the incident light which can make the interference pattern in the sample is absorbed by the photoinitiator system to produce active radicals. Then, the doped monomers are polymerized in the bright region and it causes a concentration gradient of the monomer, which then induces monomer diffusion from the unexposed dark region to the bright region. Finally, termination of propagation occurs by recombination of the radical species or some chain transfer reactions. The refractive index modulation arises from the compositional difference of the molecular chain density in adjacent two regions. After irradiation of the excitation light, the polymer binder and a newly formed polymer are just blended under physical interaction in the constructive region.

However, the monomers undergo restriction of migration under interference when its molecular size is too big. Usually when we doped the diacrylate into the cellulose acetate butyrate, the diffraction efficiency was observed around 50-60% depending on the monomer concentration and the light intensity. Therefore, we made much attempt to prepare the photopolymer exhibiting the higher diffraction efficiency with good light sensitivity and its stability.

The way to improve the diffraction efficiency of the photopolymer is the addition of small amount of plasticizer. It was already suggested that the plasticizers enhance monomer diffusion to increase the diffraction efficiency and its stability.[14,15] H. Yao *et al.* [14] investigated the effect of the plasticizer on the diffraction behavior of the photopolymer. Their formulations include a small amount of (0.4%) of TEA as a charge transfer agent that possesses some plasti-

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cizing effect. In order to study the influence of a higher plasticizer concentration precisely, they added 2% of glycerol or dimethylsulfoxide to the PP solution. They believed that the plasticizers enhance monomer diffusion during and after exposure although no glass transition temperature change was investigated. They obtained diffraction efficiency higher than 70-75% using PVA based photopolymer. Owing to the plasticizer, long term stability of photopolymer was highly improved and crystallization tendency was much prevented.

Dendrimer can play two important roles for a highly efficient photopolymer. One can be used as a PP binder since they have inherent voids to occupy the monomer and to provide large free channels for monomer diffusion. They also have reasonably high T_g and good film forming property. It helps to improve monomer migration efficiency and then induces high refractive modulation between the dark and the bright region. The other function of dendrimer is plasticization when it is doped in the rigid polymer matrix. When we doped the dendrimer in the thermoplastic binder, it can loosen the polymer chains to make the monomer diffusion much more effectively.

In this study, we synthesized the dendrimer that is useful either as a binder or as a plasticizer for the new photopolymers. The Fréchet type dendrimer was designed and synthesized for fabricating the photopolymer thick films.[16] The other additives for preparing the photopolymer films were bisphenol A ethoxylate diacrylate (DA, M_n=512, n=2), HABI, MBOZ, and DEAW that are already known in the literature.[17,18]

We studied the diffraction properties of the gratings fabricated in our photopolymer systems, which were investigated by real-time optical recording.

Experimental

The synthetic procedures for the dendrimers used herein were depicted in Figure 1.

The intermediate compounds for the dendrimer-I were synthesized following the known method after minor modification.[18]

Synthesis of Dendrimer-I. 1,3-Bis-benzyloxy-5-bromomethyl-benzene (12.0 g, 31.3 mmol), 1,1,1-tris(4-hydroxyphenyl) ethane(3.20 g, 10.4 mmol), (11.0 g, 78.3 mmol) and a catalytic amount of 18-crown-6 (0.30 g, 1.13 mmol) were dissolved in 250 mL of dried acetone under argon. The reaction mixture was stirred at 70 °C for 48 hrs. The resulting mixture was filtered and the organic layer was diluted with 200 mL of chloroform and washed with 500 mL of water several times. The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo* after filtration. The resulting product was purified by silica gel column chromatography (methylene chloride: hexane = 7:3) to yield 8.9 g (68%) of white solid.

^{1}H NMR (300 MHz, $CDCl_3$) : δ(ppm) 2.01 (s, 3H), 4.96 (s, 6H), 5.07 (s,12H), 6.60 (s, 3H), 6.67 (s, 6H), 6.86 (d, J=9.0 Hz, 6H), 6.90 (d, J=9.0 Hz, 6H), 7.42-7.26 (m, 30H)

υ_{max}(film on KBr)/ cm^{-1}, 2925, 1605, 1593, 1484, and 1245

Synthesis of Dendrimer-II. Dendrimer-I (5 g, 4.12 mmol) was dissolved in dried tetrahydrofuran (300 mL). 10% Pd/C (1.3 g, 12.2 mmol) and cyclohexene (65 mL) were added in the mother solution. The reaction mixture was kept stirring at 75 °C for 36 hrs. The solution was filtered and the filtrate was concentrated. The resulting product was purified by silica gel column chromatography (ethanol: methylene chloride = 1:9) to yield 1.7 g (63%) of white solid.

^{1}H NMR (300 MHz, DMSO-d_6, rt) : δ(ppm) 2.63(s, 3H), 4.86(s, 6H), 6.11(s, 3H), 6.25(s, 6H), 6.84(d, J=9.0 Hz, 6H), 6.89(d, J=9.0 Hz, 6H), 9.25(s, 6H)

υ_{max}(film on KBr)/ cm^{-1}, 3528, 2930, 1600, and 1598

Preparation of the Photopolymers. We prepared three photopolymers for studying the diffraction behaviors. PP-1 and PP-2 are composed of dendrimer (I or II) as a binder.

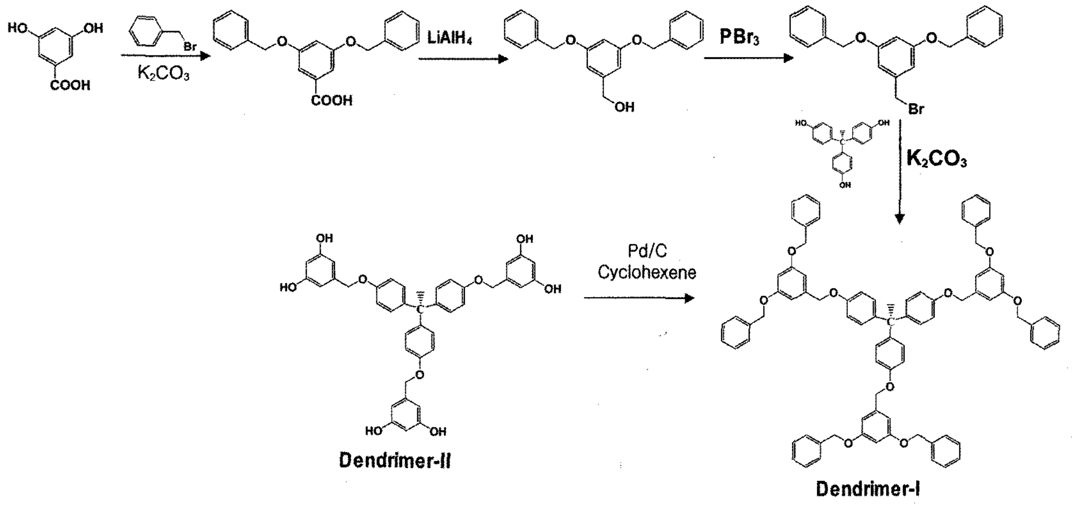

Figure 1. Synthetic procedure for the dendrimer-I and II.

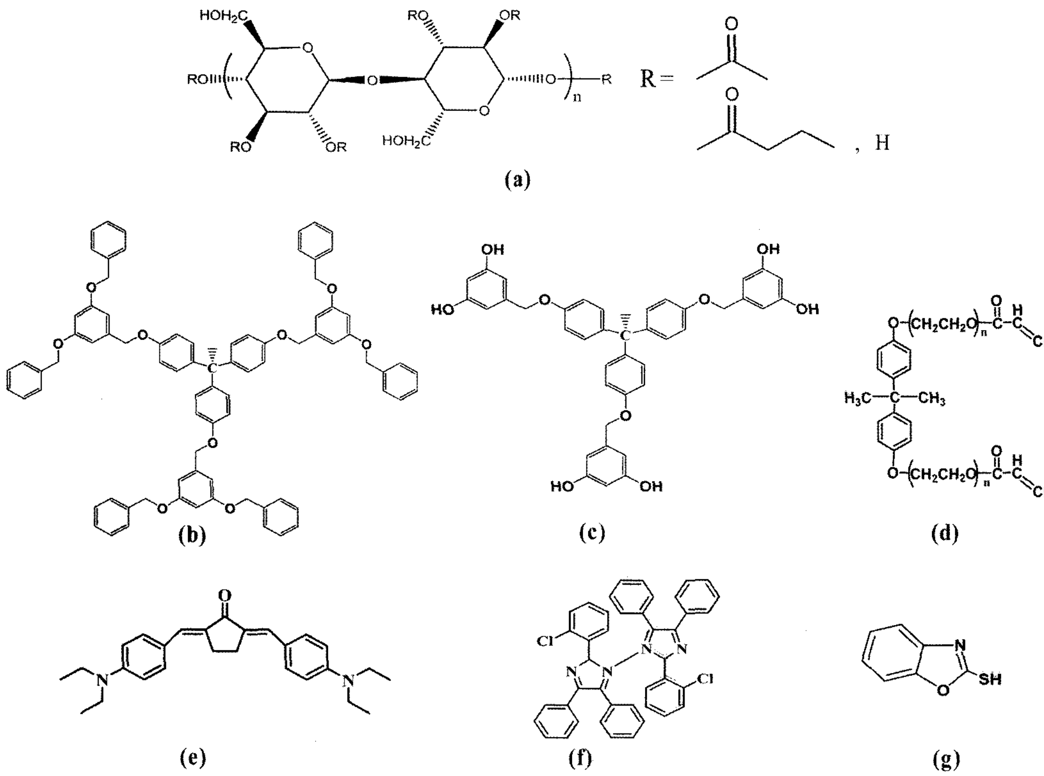

Figure 2. The chemical structures of the polymer binder, the monomers, and other additives. (a) cellulose acetate butyrate (CAB), (b) dendrimer-I, (c) dendrimer-II, (d) bisphenol A ethoxylate diacrylate (DA), (e) 2,6-bis(4'-diethylaminobenzylidene)cyclopentanone (DEAW), (f) hexaarylbiimidazole (HABI), and (g) mercaptobenzoxazole (MOBZ).

PP-3 was made of cellulose acetate butyrate (acetyl: 2%, butyryl: 52%, M_n=30,000) binder without dendrimer and PP-4, with dendrimer as a plasticizer.

The compounds were formulated in tetrahydrofuran (THF) and the solution (conc: 20 wt%) was cast on the borosilicate glass using a doctor blade. In Figure 2, all compounds for preparing the photopolymers are shown including the initiating species. In our experiment, the thickness of the photopolymer film was set about 60 μm that was measured by Surface Profilometer (KOSAKA, ET-3000). Infrared spectrum was recorded with attenuated total reflection method (Harricks ATR-single reflection diamond, Perkin Elmer FTIR). Spectroscopic ellipsometry measurement to determine the refractive index was performed with incidence angles of 65, 70, and 75 degrees using a Woollam VASE model with autoretarder in the spectral range of 400-900 nm (1.3-3.1 eV). The capability of multiple angles of incidence increases the accuracy in determining the layer dielectric function out of pseudo-dielectric functions. The *pseudo*-dielectric functions were fitted using non-linear Levenberg-Marquardt algorithm using WVASE32 software.

Measurement of the Diffraction Efficiency. Argon laser (λ=514 nm) was used in recording and He-Ne laser (λ=632.8 nm) was used to probe the recorded grating. The beam was expanded using a microscope objective and a spatial filter. The pump beams were passed through a spatial filter to make planar collimated light. Two vertically plane polarized (s- & s-) light beams with an equal intensity were obtained by adjusting the quarter wave plate and the polarizers appropriately, fabricating the holographic grating. The basic principle of recording gratings was based on optical interference.[19,20] The intensity pattern consists of bright and dark planes throughout the region of the intersection. This provides a refractive index grating in the material by diffusion and photopolymerization of the monomer. The angle between the interferential two beams is set to be 2θ= 28°. Time-resolved variation of the 1st-order diffraction was monitored on-line with a probe beam from a He-Ne laser (*p*-polarized I=0.1 mW/cm^2). Standard lock-in detection techniques were used to maximize the signal-to-noise ratio. (Lockin-amplifier, EG&G 7260 DSP; Optical chopper, SR540, 4 Hz-3.7 kHz).

The probe beam was diffracted by the gratings with an efficiency η that is defined as the ratio of the intensities of the diffracted to the incident beam ($\eta=I_{diff.}/I_o$).

Results and Discussion

The macromolecular binder is a very important component affecting physical properties of the photopolymer, such as its rigidity, environmental stability, dimensional stbility, and maximum achievable thickness. It also affects the diffusion property of the doped monomers as well as the photoinduced refractive index change. In conventional photo-polymers, the photoinitiating species and the monomers are typically dispersed uniformly in a thermoplastic binder. The polymer binder having relatively low T_g and a newly formed polymer are just blended physically by virtue of the molecular specific interaction. In this work, we expected that the dendrimer binder can facilitate monomer diffusion process due to their large void between the arms and that plasticization in the usual thermoplastic polymer binder can enhance the diffraction efficiency.

Synthesis of Dendrimer I and II and Photopolymer Preparation. We employed 1,1,1-tris(4-hydroxyphenyl) ethane as a core molecule that can have three dendrons(see Figure 1). Following the synthetic procedure, we reacted 3 equivalent of 1,3-bis-benzyloxy-5-bromomethyl-benzene with the core molecule to produce dendrimer-I in the presence of potassium carbonate. Using Pd/charcoal, we deprotected benzyl group to give hydroxy-terminated dendrimer-II. Deprotection reaction was successfully performed at 75 °C to give a high yield (>63%). The structures of the dendrimers were confirmed by NMR spectroscopy(see Figure 3). Dendrimers are quite soluble in acetone, tetrahydrofuran, tetrachloroethane etc.

All additives such as the monomer, HABI, MOBZ, and DEAW in photopolymer were also well soluble in tetrahydrofuran for casting the thick film. In order to remove the residual gas in the solution, the solution was kept under vacuum for 5-6 hrs before usage. The thick film was well fabricated by a doctor blading method controlling the rate of solvent drying in the leveled desiccator at room temperature. The thickness of the film was measured to be about 60 μm, determined by Surface Profilometer. The typical composition of the photopolymer is as follows: 0.5 g of dendrimer binder: 0.23 g of monomer: 0.014 g of HABI: 0.008 g of MOBZ: 0.004 g of DEAW. We chose the optimized composition of photopolymer, suggested in the literature.[17,18]

ATR-FTIR Spectroscopic Study on the Photopolymer Films. We recorded the ATR-infrared spectra of the photopolymer (PP-1) film samples composed of dendrimer-I binder before and after visible light irradiation as shown in Figure 4. Generally, the double bond stretching absorbance in diacrylate oligomer (DA) at 1607 and 1595 cm^{-1} decreased to some extent accompanying with the other combination bands. This indicated that diacrylates underwent the polymerization partially by irradiation of the visible light. About 66% of conversion was achieved in the light treatment. Therefore, the monomers we doped are partially polymerized under 514 nm visible light irradiation in the presence of the radical photoinitiating species (HABI/MOBZ) sensitized by

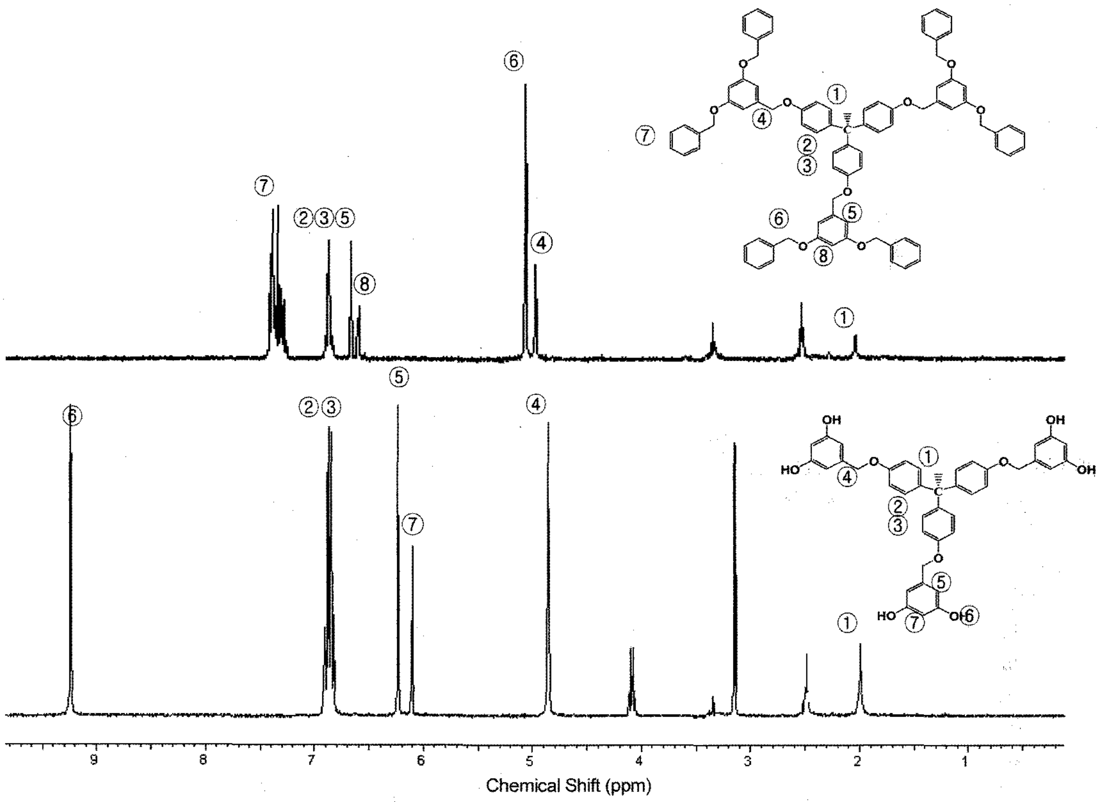

Figure 3. NMR spectra of the dendrimer-I and dendrimer-II.

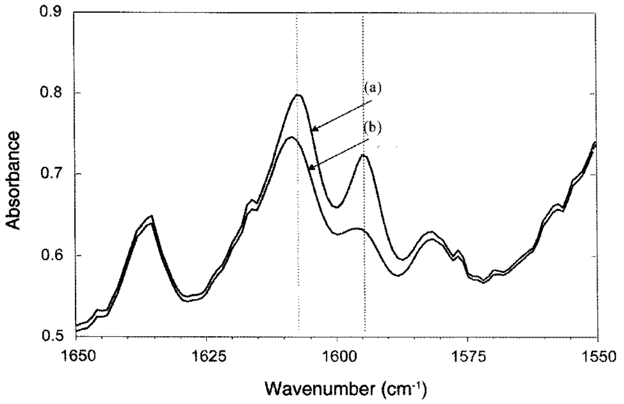

Figure 4. ATR FTIR spectra of the PP-1 sample before (a) and after (b) light illumination.

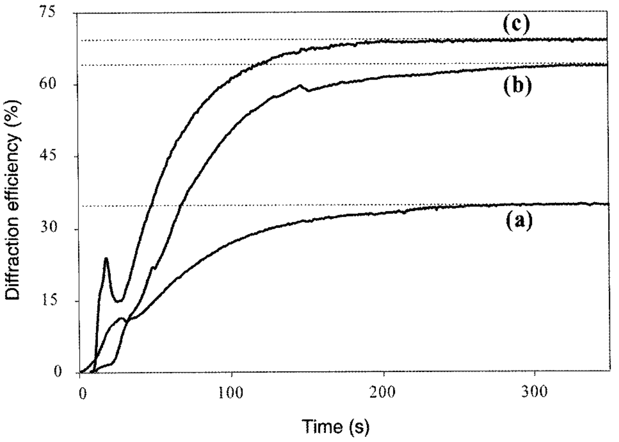

Figure 5. Variation of the diffraction efficiency of the PP-1 with the light intensity.

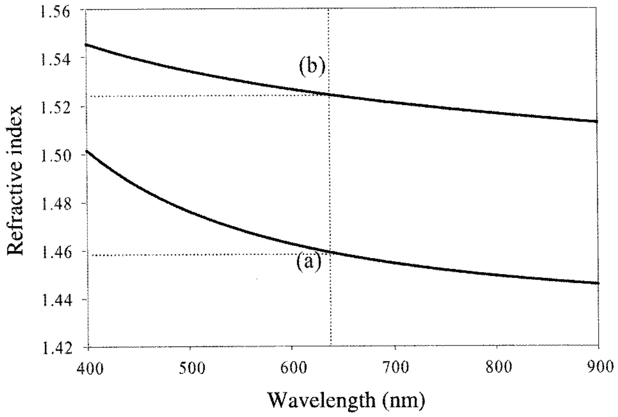

Figure 6. Variation of the refractive index of PP-1 before (a) and after (b) light illumination.

DEAW.[21]

Diffraction Behavior of the Photopolymer Consisted of the Dendrimer Binder. Firstly, we fabricate the PP-1 using the dendrimer-I, the diacrylate monomer, and the initiating species. PP-2 prepared with dendrimer-II instead of dendrimer-I, was employed for comparison of the diffraction behavior. The concentrations of all additives are identical.

We studied the diffraction response of the refractive index grating using the prepared photopolymers (PP-1 and PP-2) to estimate the light sensitivity. Figure 5 shows the dynamic behaviors of the diffraction efficiency of PP-1 with the writing beam intensity. It is clear that the diffraction efficiency increases with the light intensity. Under light intensity of 32 mW/cm^2, 69-70% of the maximum diffraction efficiency could be observed in this experiment. The sharp peak around 20 sec in curve (c) can be conjectured due to nonuniformity of the monomer in the photopolymer. However, the PP-2 made of dendrimer-II did not show the diffraction behavior at all, which is mainly attributed to the radical inhibition from the six phenolic protons in the hydroxy terminal groups.

We measured the refractive indices of the photopolymer samples, PP-1 before and after excitation light illumination using the ellipsometric technique. We also measured the indices of the PP-1 before and after light irradiation (see Figure 6). The index after light illumination is much higher than that of the previous sample. The indices of the PP-1 at 632 nm before and after irradiation were determined around 1.4584 and 1.5246, respectively. The difference of the index is about 0.0662 at 632 nm, which is significantly higher after light irradiation. The diacrylate oligomers were polymerized themselves so that the light treated photopolymer can be composed of the highly dense structure. Thus, we confirmed that the photopolymerization could occur under the irradiation of the optimized light dose we selected. Therefore, the dendrimer-I we synthesized can behave as an efficient binder for the photopolymer likewise the thermoplastic polymer binder in the conventional photopolymer.

Diffraction Behavior of the Photopolymer Consisted of the Cellulose Acetate Butyrate with the Dendrimer as a Plasticizer. We investigated another function of the dendrimer-I after mixing it into the thermoplastic polymer binder of cellulose acetate butyrate (CAB). CAB has T_g around 130 °C. The sample with 1 wt% of dendrimer showed 122 °C of T_g. When introducing only 1 wt% of dendrimer-I into the CAB, we could observe significant increase of the diffraction efficiency. We can expect the efficient migration of the monomer under optical interference owing to the plasticizing effect.

PP-3 was composed of CAB binder only including the other additives. PP-4 was prepared with CAB doped with 1 wt% dendrimer-I. T_g of PP-3 was observed around 114 °C whereas PP-4 has T_g around 108 °C. The compositions of the additives are identical in two photopolymers. The basic composition of the photopolymer is as follows: 0.5 g of CAB binder: 0.23 g of DA monomer: 0.014 g of HABI, 0.008 g of MOBZ, 0.004 g of DEAW. The light intensity for

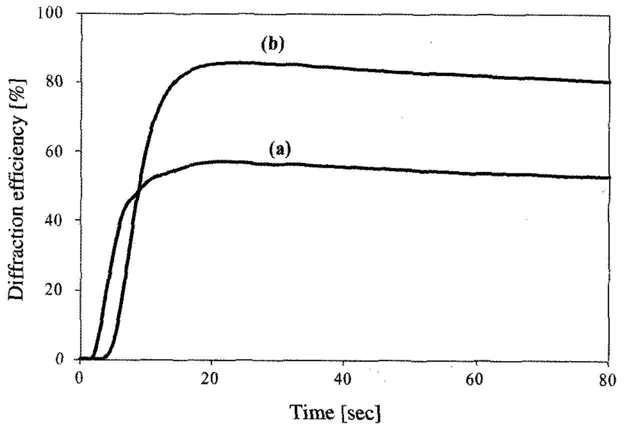

Figure 7. Variation of the diffraction efficiency of PP-3 and PP-4. (a) PP-3: CAB binder only and (b) PP-4: CAB+1 wt% of dendrimer-I.

the comparison of the dynamic behaviors of the diffraction efficiency was selected to be 32 mW/cm^2.

In Figure 7, we can observe the diffraction behavior of the PP-3. The saturated diffraction efficiency was determined around ~55%. However, once we doped the dendrimer into the CAB binder, the diffraction efficiency increased significantly under an identical condition of light illumination. It showed around 80-83% of the diffraction efficiency. This is partially due to the existence of the dendrimer in the PP matrix. We conjecture that the dendrimer-I played as an effective plasticizer to loosen the polymer chains and increase the free volume of CAB although no clear evidence of the physical property is available. Then, the monomer diffusion was facilitated to increase the concentration of the polymerizable monomers in the bright region. However, when we dope 3 wt% of dendrimer in CAB, the diffraction efficiency becomes lower, which is likely due to higher degree of backward migration of the polymer chain. Therefore, 1 wt% doping concentration of the dendrimer-I was estimated as the optimum concentration to show highest diffraction efficiency in this formulation.

We make our efforts to synthesize the photoreactive dendrimer containing the acrylate group at the periphery and apply them to develop new IPN type photopolymers.

Conclusions

New photopolymers (PPs) were prepared and the holographic gratings were fabricated in film samples by the optical interference method. The dendrimer binder showed good feasibility for utilizing it for photopolymer. The PP with a dendrimer binder showed the improved diffraction behavior that is comparable to the thermoplastic binder PP system. Dendrimer-I played an important role of the plasticizer for lowering T_g and enhancing the diffraction efficiency of the photopolymer. Thus, we evaluate that the dendritic molecules are very useful for photopolymer fabrication because of inducing highly efficient monomer diffusion and the higher rate of polymerization in the bright region. If we impose higher stability of the diffraction efficiency and the dimensional stability during light exposure, we may utilize the dendrimer based PP for holographic device system in real application.

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