1

Ionic Liquids in Photopolymerizable Holographic Materials

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1. Introduction

A variety of materials have been used to record hologram, such as silver halide emulsions, hardened dichromated gelatin, ferroelectric crystals, photochromics, photoresist, photodichroics and photopolymerizable materials [1-3]. Photopolymerizable holographic materials due to their low cost and dry processing have attracted great interest in academics and industry. They have broad applications in holographic memories, recording media, LCD displays, helmet-mounted display, optical interconnects, waveguide couples, holographic diffusers, laser eye protection devices, automotive lighting, and security holograms. The photopolymerizable holographic composite contains mainly a matrix binder, a photopolymerizable monomer, an initiator system, a plasticizer and additives [4-17]. Due to the inter diffusion of the unpolymerized monomers in a holographic film, areas with high and low refractive index are formed during the irradiation with an interference pattern. Many photopolymer systems have been developed including binary photopolymer composites, organic-inorganic nanocomposites, a hybrid organic-inorganic host consisting of porous glass, and a system using monomers capable of cationic ring-opening polymerization.

The addition of a plasticizer or an additive can increase the refractive index modulation and the final diffraction efficiency. Monroe et al. reported that tri(2-ethylhexyl)phosphate, glyceryl tributyrate, polyethylene glycol or functional polyethylene glycol etc. as plasticizers may increase the refractive index modulation [18]. Frank recommended photopolymerizable compositions with triglycerides as additives, which provide a stable holographic material with high refractive index modulation [19]. Tucker et al. used trithiocarbonate as additive to increase the diffraction efficiency, uniformity and reproducibility in the formation of electrically switchable holographic gratings [20]. Finally, one publication reports about an additive to improve the sensitivity of photopolymerizable hologram material [21].

Ionic liquids are organic salts that are liquid at ambient temperatures, preferably at room temperature. They are nonvolatile, thermally and chemically stable, highly polar liquids, high ionic conductivity, large electrochemical window and ease of solubilization of a large organic molecules and transition metal complexes [22-25]. Applications of ionic liquids include their use in synthesis, catalysis, separation, electrochemistry, electrolytes, lubrication, biomass processing, drug delivery and others. The cations of ionic liquids are

often large organic cations, like imidazolium, pyridium, piperidium, pyrrolidium, quaternary ammonium, phosphonium, pyrrolidium or pyrazolium etc. The anionic parts can be organic or inorganic anions such as some halides, nitrate, acetate, hexafluorophosphate, tetrafluoroborate, trifluoromethylsulfonate, or bis(trifluoromethanesulfonyl) imide etc (Figure 1). Many combinations of organic cations with different counter anions are already known, and the properties of ionic liquids may be adjusted by the proper selection of the cation and counter anion. The number of possible cation-anion combinations is greater than one million, thus allowing the design of tailor-made ionic liquids for a desired task.

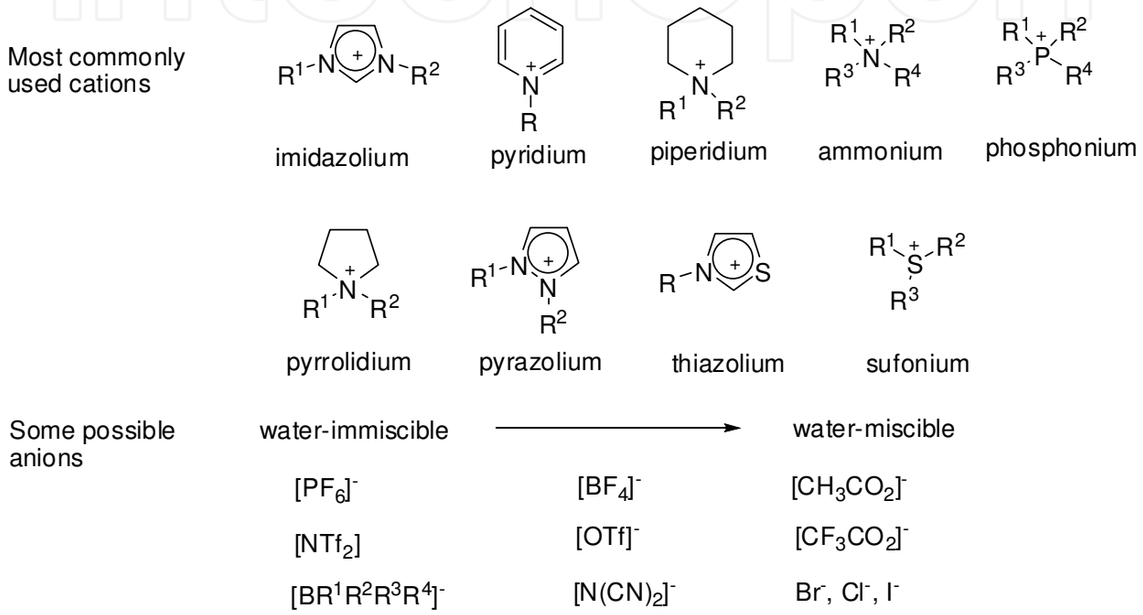

Fig. 1. Chemical structures of typical ionic liquids.

Ionic liquids have also attracted the attention of polymer chemists [26-30]. Ionic liquids have been used as reaction media in several types of polymerization processes, such as free radical polymerization [31, controlled radical polymerization [32-33}, ring-opening polymerization [34], anionic/cationic polymerization [35], enzymatic polymerization [36], and microwave-assisted polymerization [37] and electrochemical polymerization [38]. The applications of ionic liquids provide several advantages. For instance, in radical polymerization, the k_p/k_t ratio (where k_p is the rate constant of propagation and k_t is the rate constant of termination) is higher than in organic media, and thus better control of the process can be achieved [32-33]. Under mild reaction conditions, the catalytic system can be recycle used [39]. Higher yields [40], high enzyme activity [41], high conductivity polymers [42], etc., have been reported. Ionic liquids have been used as plasticizers of various kinds of polymers [43-44], as templates for porous polymer synthesis [45-46], and as key components in new classes of polymer gels [47-49]. Polymerizable ionic liquids were used to synthesize ionic liquid co-polymers for the applications in ion-conductive polymer film [50], nanostructured liquid crystalline hydrogel [51], or microwave-absorbing polymer composite [52], etc.

Recently, we have explored a new application of ionic liquids in photopolymerizable holographic materials [53-55]. In the chapter, we highlighted our research in detail. The

photopolymerizable holographic materials with higher sensitivity, higher resolution and higher diffraction efficiency were synthesized using ionic liquids as additives, which present strong dark diffusion of the monomers during the polymerization process. The materials have been used in fabricating optic diffuser for Liquid-Crystal Displays (LCD). The symmetric and asymmetric diffusers with directional diffusion property were achieved.

2. Experiment

All chemicals were used as received. Ionic liquids were synthesized according to the literature methods [56] or received from IoLiTec GmbH. Poly-(ethylenglycol)-methacrylate (PEGDMA) (average Mn ~ 330) was ordered from Sigma-Aldrich Co., Epoxy L20 and Hardener 3261 from R&G Faserverbundwerkstoffe GmbH. Irgacure 184 was a gift of Ciba Specialty Chemicals (Pty) Ltd. Scanning electron microscopy (SEM) imaging was performed on a JEOL JSM 6400F (JEOL Germany GmbH, Eching, Germany). Optic microscopy imaging was taken with Olympus BH2 equipped with a CCD camera.

2.1 Fabrication of the transmission holographic gratings

The transmission holographic grating was created by means of two-wave interference [57]. The set-up is shown in Figure 2. An argon ion laser was used here as coherent light source. The laser beam with a wavelength of 351 nm of (*power* ~ 32 mW cm^{-2}) was split by a beam splitter into two subsidiary beams of equal intensity and adjusted to obtain an interference pattern on the sample. The beam diameter was about 3 mm. Using He-Ne laser (633 nm) as reference light, the generated first-order light was read with a Lock-in Amplifier M850. The exposure time was controlled by an electronic shutter. The diffraction efficiency (η) was calculated from the ratio of the intensity of the first order laser beam diffracted by the hologram structure (I_1) to the incident intensity I_0 (to minimize the absorption and the scattering effect, I_0 was the incident intensity through the blank sample), $\eta = I_1/I_0$. Several drops of the composite were placed on a glass slide with two pieces of aluminium foil (10 μm) as spacers, on which another glass slide was placed afterwards. By gentle pressing, the drops spread between the two plates to obtain a layer with a thickness of about 10 micrometers. Then the film was exposed to a two-beam laser to create the hologram (the angle between the two beams was 2^o and the grating space was approx. 10.0 μm). Other special frequency gratings were fabricating in the similar procedure except to change the angle between the two laser beams.

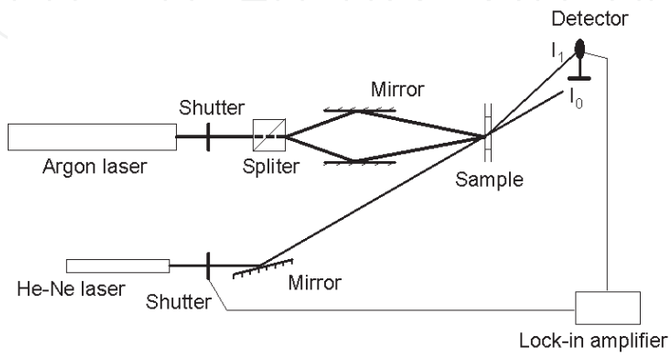

Fig. 2. The optic set-up for the hologram recording.

2.2 The fabrication of optic diffuser

Oriel® Flood Exposure Source (Model 92540-1000, Newport Co.) was used as the UV source. An optic setup was shown in Figure 3. A textured mask with random 2-15 micrometer apertures was used as mask, and polyester (PET) film was used as substrate. 75 μm thickness PET film was used as spacer. The films of photopolymerizable holographic materials were exposed vertically or 60° to collimated UV light through the mask, followed by exposing from another side to complete the polymerization process. The direct transmittance versus the tilt angle was measured with Haze meter (BYK Gardner) and the diffuser was rotated from -60° to +60° around the vertical axis.

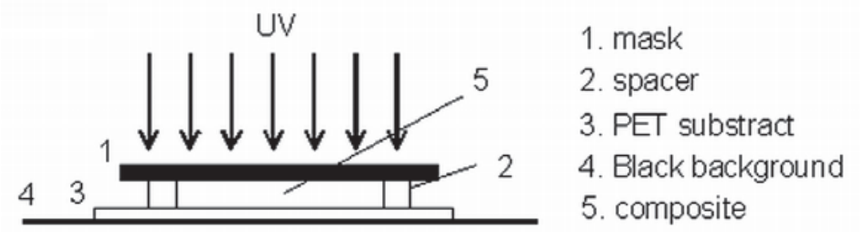

Fig. 3. The optic set-up for fabricating optic diffuser.

3. Results and discussion

3.1 The influence of ionic liquids on photopolymerizable holographic materials

Ionic liquids have significant influence on the kinetics of various polymerization reactions [26-27]. The nature of ionic liquids has strongly influenced the polymerization rate and conversion of oligomer. For instance, Chesnokov et al. reported that the addition of imidazonium salts suppress the polymerization of PEGDMA, however, tetraalkylphosphonium salts improve the photopolymerization [58]. Photopolymerizable holographic materials for practical use need to have high sensitivity, high diffraction efficiency and high resolution. The sensitivity of photopolymerizable holographic material and the photopolymerization rate have different meanings. The sensitivity here is defined as the needed exposure time (or energy) to reach the highest diffraction efficiency. The overall rate of polymerization (R_p) is considered as the rate of disappearance of monomer with respect to time, -d[M]/dt. In our research, we investigated the influence of ionic liquids on the sensitivity, the diffraction efficiency and the resolution of the photopolymerizable holographic materials.

Poly(ethylenylglycol)dimethacrylate (PEGDMA) (average Mn~ 330) was used as monomer, and Irgacure 184 (Irg184) was used as photoinitiator. In some samples, polyvinyl acetate (PVAC) or Epoxy L20/Hardener EPH161 were used as polymer binders. The structures of ionic liquids used are shown in Figure 4. 1,3-dialkylimidazolium, pyridium, and phosphonium with various counter anions were used as additives.

Due to the low solubility of PEGDMA in some ionic liquids, such as BMIMCl, BMIMBr, $BMIMSO_3Me$, $BMIMSO_4Me$, $BMIMSO_3Ph$, and $BMIMHSO_4$, BPMCl, $BPMPF_6$, Bu_4NPF_6, etc, PEGDMA cannot be solved fully in these ionic liquids to form homogenous composites. Table 1 collects the test composites used to record holographic gratings. Figure 5 shows the representative diffraction pattern by probing the hologram with 633 nm He-Ne laser beam. The diffraction efficiencies of the gratings are showed in Table 1 (the angle between the two beams was 2°). Although PEGDMA with IRG184 as initiator gave rise to low diffraction

efficiency (Table 1, Sample 1), most of the tested samples gave rise to good diffraction efficiencies (η) except the composites with $BMIMNCN_2$, BMIMSCN or $BMIMFeCl_4$ as additives (Table 1, Sample 2-20), and the formed gratings have better resolution than the sample 1 without ionic liquids (Figure 6a, b). In the presence of PVAC (polyvinyl acetate) (Table 1, Sample 21-32), the diffraction efficiency was further increased except for $C_{32}H_{68}PCl$, $C_{32}H_{68}PPF_6$ and $C_{32}H_{68}PBF_4$, which formed inhomogeneous composites with PEGDMA/PVAC. 34 % of the theoretical maximum diffraction efficiencies for thin hologram [1,2] were obtained. Using Epoxy L20/Hardener EPH161 as polymer binder, satisfying diffraction efficiencies were obtained as well (Sample 35-48). Interestingly, pholymerizable ionic liquids can also be used as additive in photopolymerizable holographic materials. The application of polymerizable ionic liquids may lead to form a more stable hologram. For instance, 1-butyl-3-vinylimidazolium tetrafluoroborate ($BVIMBF_4$) and 1-allyl-3-butylimidazolium tetrafluoroborate ($ABIMBF_4$) were used as additive of photopolymerizable holographic materials. 17% and 19% diffraction efficiency was obtained, respectively (Table 1, Sample 19, 20). Nevertheless, in the presence of PVAC, the theoretical maximum diffraction efficiencies were obtained as well (Table 1, Sample 33, 34). To test the polymerizability of ionic liquids can carry out polymerization under this exposure condition, $BVIMBF_4$ (2.0 g) was mixed with Irg184 (0.05 g) to form a composite. The hologram was formed successfully, but only gave rise to 2% diffraction efficiency.

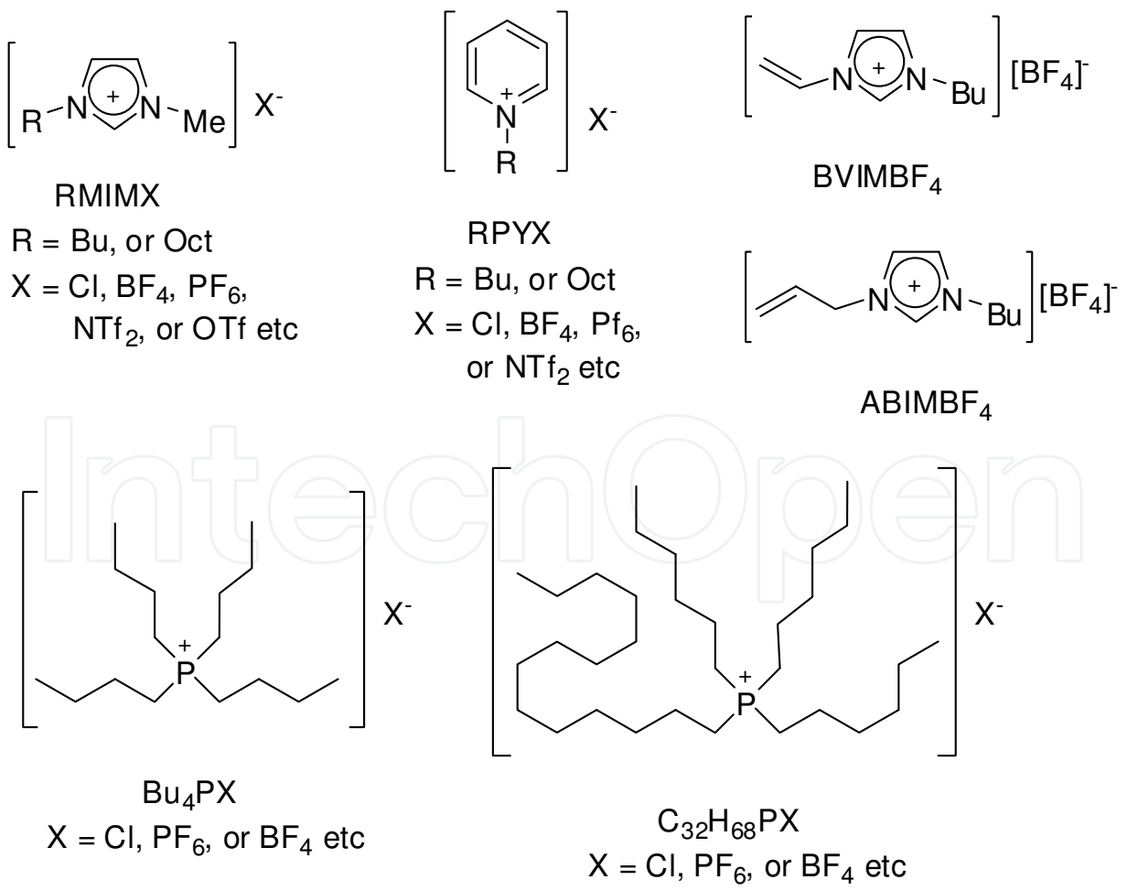

Fig. 4. Molecular structures of ionic liquids.

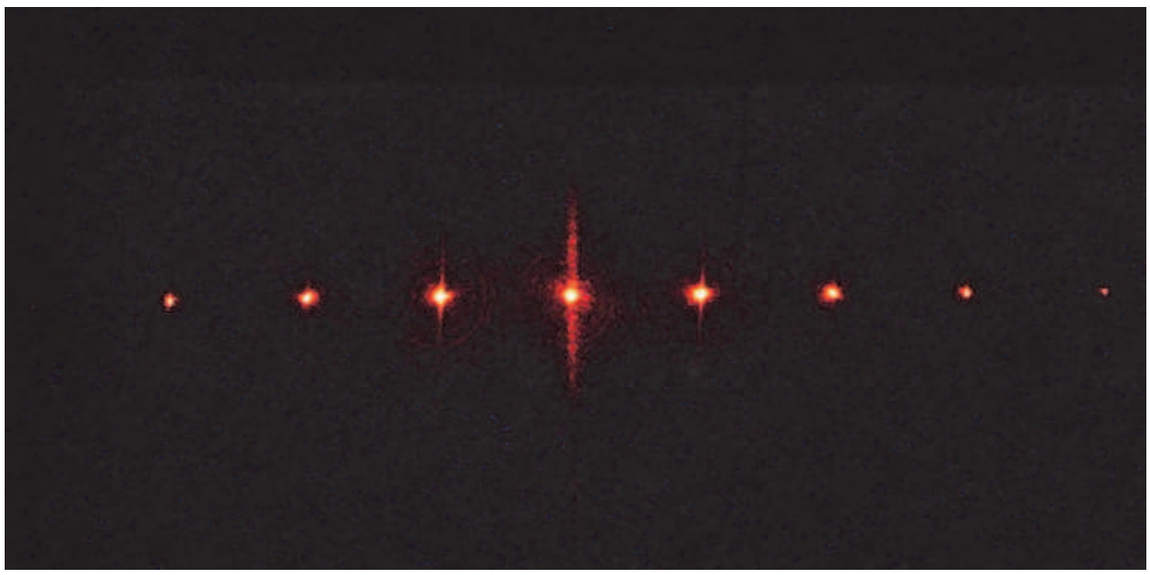

Fig. 5. The diffraction pattern obtained by 633 nm He-Ne laser beam.

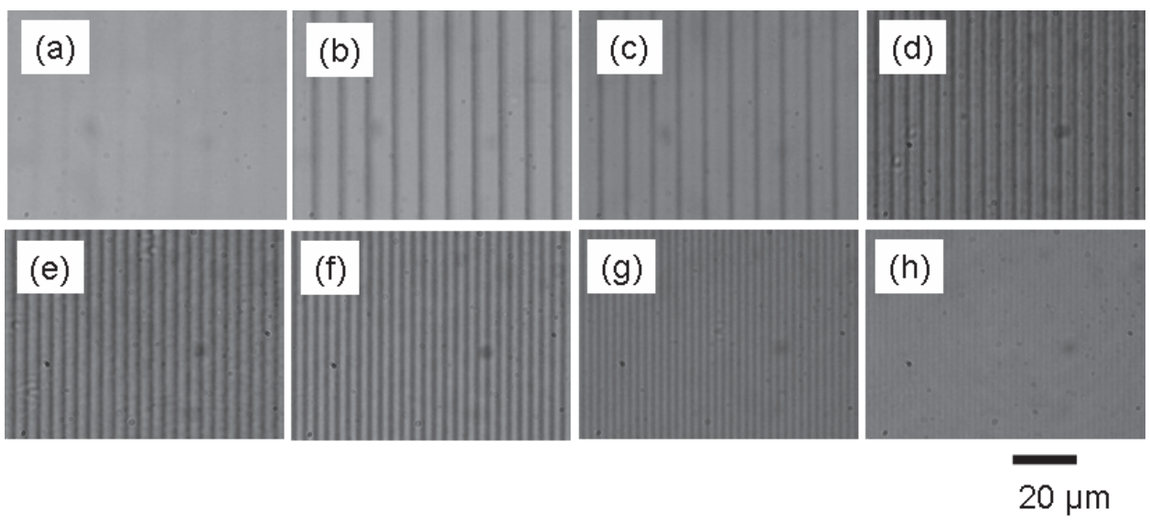

Fig. 6. Comparison of the optic microscopy images of the gratings. (a) Sample 1 (PEGDMA, 4.0g; Irg184, 0.2 g), η = 1%, Λ = 10.0 μm, θ = 1.0°. (b) Sample 2 (PEGDMA, 4.0g; $BMIMBF_4$, 1.0g; Irg184, 0.2 g), η = 16%, Λ = 10.0 μm, θ = 1.0°. (c) Sample 22 (PEGDMA/PVAC, 4.0 g, w/w = 10: 1; $BMIMBF_4$, 1.0 g; Irg184, 0.08 g), η = 34%, Λ = 10.0 μm, θ = 1.0°. (d) Sample 22, η = 14%, Λ = 5.6 μm, θ = 1.8°. (e) Sample 22, η = 11%, Λ = 4.7 μm, θ = 2.1°. (f) Sample 22, η = 8%, Λ = 4.0 μm, θ = 2.5°. (g) Sample 22, η = 3%, Λ = 2.9 μm, θ = 3.5°. (h) Sample 22, η = 1%, Λ = 2.2 μm, θ = 4.6°.

Additive	No matrix Sample[b]	DE (η, %)	With PVAC sample[c]	DE (η, %)	With EPOLH sample[d]	DE (η, %)
-	1	1	21	16	-	-
$BMIMBF_4$	2	16	22	34	35	27
$BMIMPF_6$	3	4	23	34	36	13
$OMIMBF_4$	4	13	24	31	37	24
$OMIMPF_6$	5	9	25	34	38	22
$BMIMNTf_2$	6	16	26	34	39	24
BMIMOTf	7	15	27	34	40	26
$BMIMNCN_2$	8	7	-	-	-	-
BMIMSCN	9	4	-	-	-	-
$BMIMFeCl_4$	10	1	-	-	-	-
$BMIMSO_4Oct$	11	9	28	25	41	21
$BPMBF_4$	12	22	29	34	42	20
$OPMBF_4$	13	15	30	34	43	26
$OPMNTf_2$	14	25	31	34	44	21
Bu_4PBF_4	15	27	32	34	45	29
$C_{32}H_{68}PCl$	16	11	-	-	46	4
$C_{32}H_{68}PPF_6$	17	28	-	-	47	26
$C_{32}H_{68}PBF_4$	18	15	-	-	48	20
$BVIMBF_4$	19	17	33	34	-	-
$ABIMBF_4$	20	19	34	34	-	-

[a] All of the films were exposed for 8 seconds (E ~ 0.26 J·cm^{-2}) with 351 nm Ar laser (Power ~ 32 mW·cm^{-2}). The diffraction efficiencies were measured with He-Ne laser (633 nm). The thicknesses were about 10 μm, and the grating space is about 10.0 μm. [b] PEGDMA (4.0 g), Irg184 (0.2 g), Ionic liquid (1.0 g); [c] PEGDMA/PVAC (4.0 g, w/w = 10: 1), Irg184 (0.08 g), Ionic liquid (1.0 g); [d] PEGDMA (3.4 g), Epoxy L20/Hardener EPH161 (0.5 g, w/w = 4: 1), Irg184 (0.1 g), Ionic liquid (1.0 g).

Table 1. Properties of the holographic films.[a]

Other different spatial frequency gratings were also fabricated to find that the ionic liquid-photopolymerizable holographic materials perform better at larger grating spacings. For instance, the diffraction efficiency of the grating based on composite 4 is 34% for 10.0 μm, 14% for 5.6 μm, 11% for 4.7 μm, 8% for 4.0 μm, and 3% for 2.9 μm, respectively. Figure 7 shows the spatial frequency response of the material. The spatial frequency increasing leads to the decreasing of the diffraction efficiency. These results are similar to the hologram material based on a photopolymerizable nematic acrylate [20]. Figure 6c-f shows the optic images of the gratings.

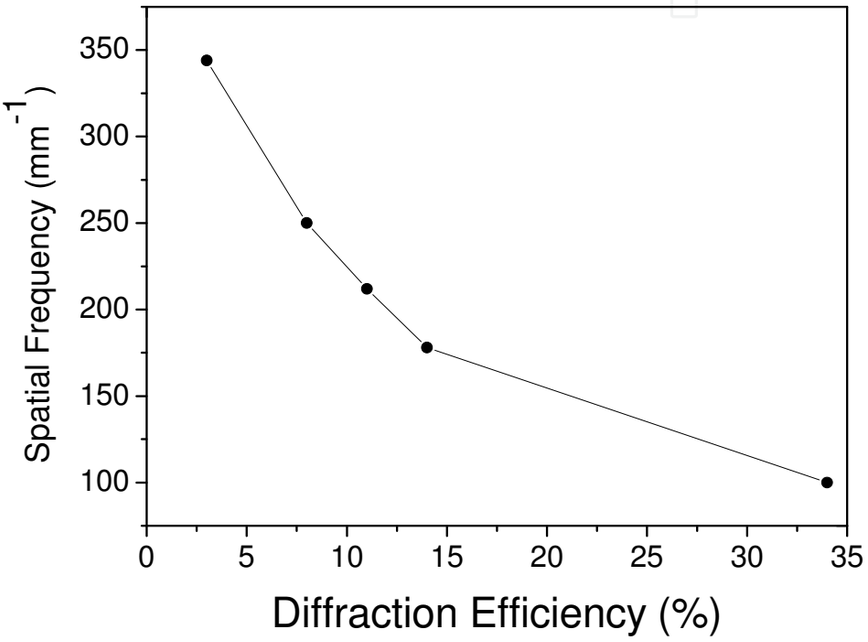

Fig. 7. The spatial frequence (mm^{-1}) vs the diffraction efficiency (%) of composite 4. The spatial frequencies increasing led to the decreasing of the diffraction efficiencies.

Figure 8 shows the representative curves of the diffraction efficiencies with reference to time. In the presence of $BMIMNCN_2$, BMIMSCN or $BMIMFeCl_4$, an unstable hologram was formed (Figure 8f). In contrast, in the presence of $BMIMBF_4$, $OMIMBF_4$, $BMIMPF_6$, $OMIMPF_6$, $BMIMNTf_2$, BMIMOTf, $BMIMSO_4Oct$, $BPMBF_4$, $OPMBF_4$, $OPMNTf_2$, Bu_4PBF_4, $C_{32}H_{68}PCl$, $C_{32}H_{68}PF_6$, $C_{32}H_{68}BF_4$, $BVIMBF_4$ or $ABIMBF_4$, the materials were more sensitive only needing about 5-6 seconds exposure to reach the maximum stable value and had higher diffraction efficiencies (Figure 8 b-e) compared to the composite in the absence of ionic liquid needing about 8 seconds exposure (Figure 8 a). The diffraction efficiency continued to increase to a stable value after stopping the exposure (Figure 8 b-e). According to the diffusion theory for formation of the hologram, the concentration of the monomer (c) is related to the diffraction efficiency (I/I_0): $-dc/dt = kIc$, whereas k depends on the extinction of the quantum yield [59]. For the composites without ionic liquid or with $BMIMNCN_2$, BMIMSCN, or $BMIMFeCl_4$ as additive, the diffraction efficiencies first increase, then drop sharply (Figure 8a, f), which indicates that the diffusion rate is bigger

than the polymerization rate at the beginning. At the end triggered by the monomer concentration, the diffusion rate is less than the polymerization rate. This has an impact on the diffraction efficiency. In the presence of some ionic liquids, such as $BMIMBF_4$, $BMIMPF_6$, $OMIMPF_6$, $BMIMNTf_2$, $BPMBF_4$, etc, the diffraction efficiencies increased continually during the hologram formation (Figure 8b-e), which indicates that the diffusion rate is higher than the polymerization rate during the polymerization process. For the formation mechanism of the hologram it can be proposed that, a monomer is polymerized in the exposure region by light activation while writing the information into the material. Since the concentration of

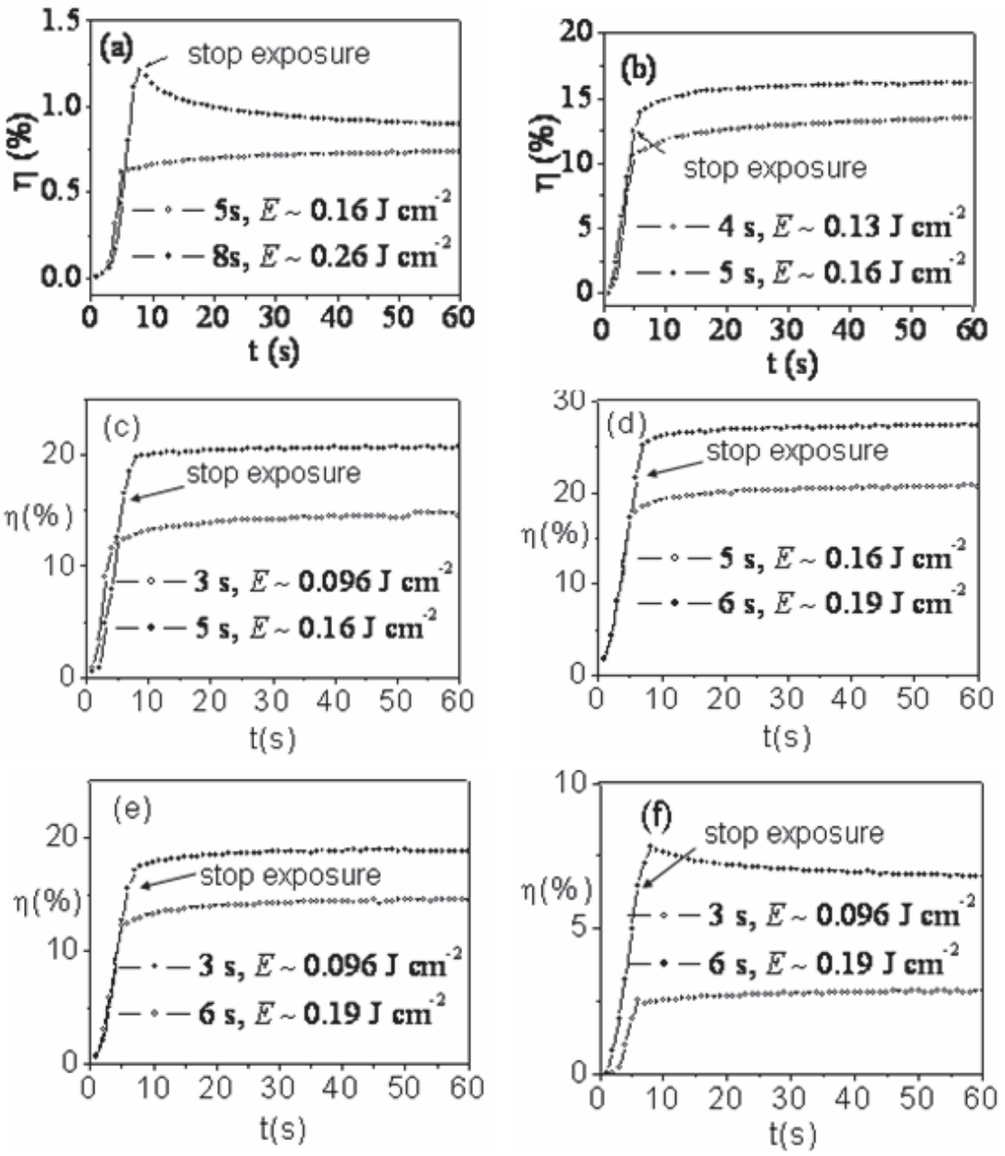

Fig. 8. The diffraction efficiency (%) vs time (second). The power of the laser beam is approximately 32 mW·cm-2. The different exposure time may be seen from the different mark of the skeleton. (a) Sample 1; (b) Sample 2 ($BMIMBF_4$); (c) Sample 12 ($BPMBF_4$); (d) Sample 15 (Bu_4PBF_4); (e) Sample 20 ($ABIMBF_4$); (f) Sample 8 ($BMIMNCN_2$).

the monomer is reduced, monomers in the dark and unexposed regions of the material diffuse to the exposed region. Due to the diffusion-controlled polymerization in the presence of some ionic liquids, the diffraction efficiencies increase continually during the hologram formation. This gives rise to higher diffraction efficiencies and bigger refractive index modulations compared to the other composites, whose diffraction efficiencies first increase, then drop sharply because of the polymerization rate controlled polymerization. On the other hand, the characters of ionic liquid have important effect on the properties of photopolymerizable holographic materials. For example, although both [BMIM][BF_4] and [BMIM][PF_6] can improve the sensitivity of the materials, only the former gave rise to high diffraction efficiency. This may be due to the different solubility property, viscosity or polarity of ionic liquids [27].

Additionally, we have also looked after the morphology of the gratings with scanning electron microscopy. In absence of polymer binder, sample 2 gave rise to a homogeneous grating, where we can not find any obvious phase separation (Figure 9a). But in the presence of epoxy resin, an obvious phase separation occurs which forms droplets of approx. 1.5 μm on the grating (Figure 9b). Possibly these are due to the different solubilization of polymers in ionic liquids [60,61]. Phase separation is often seen in the holographic polymer dispersed liquid crystal (H-PDLC) [62,63].

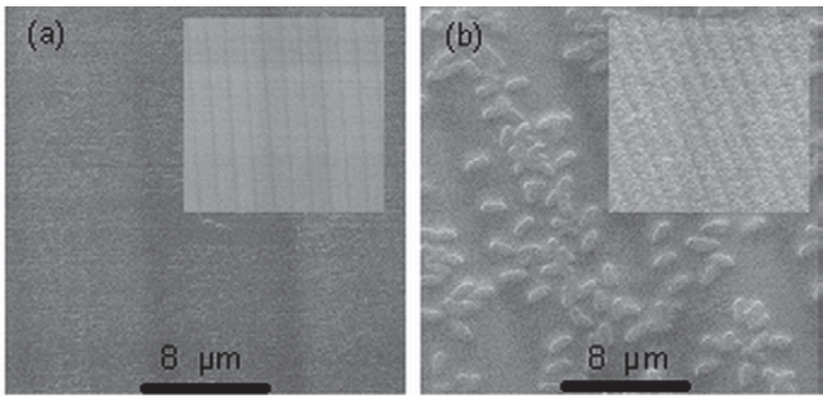

Fig. 9. SEM micrographs of the gratings. (a) sample 2 (PEGDMA, 4.0g; $BMIMBF_4$, 1.0g; Irg184, 0.2 g), (b) sample 35 (PEGDMA, 3.4 g; Epoxy L20/Hardener EPH161, 0.5 g, w/w = 4: 1; Irg184, 0.1 g, $BMIMBF_4$, 1.0g).

3.2 Fabricating optic diffuser using photopolymerizable holographic materials

Optic diffusers are key optic elements in liquid crystal displays (LCDs) which spread the incident light from sources over a wide angle to prevent light sources from being seen directly by viewers and to keep the brightness uniform over the entire display area. Generally, the diffusers can be classified into two types: the particle-diffusing type or the surface-relief type. Particle diffusers rely on the transparent beads inside the plastic films of plates to scatter light [64-66]. The distribution of diffusing beads in the diffuser is non-uniform, which affects the performance of diffusion light. The surface-relief diffusers scatter the light by the microstructures thereon, e. g. microlens diffuser [67,68], random phase diffuser [69], deterministic diffractive diffuser [70] and holographic diffuser [71-77]. Much research has been focused on holographic diffusers, which were produced via exposure of the film of photopolymerizable holographic material to collimated light through a diffuser

source or mask. Comparing to other diffusers, the holographic diffusers have unique properties, such as controllable diffusion angle, directional property, volume refractive index variation and high transmittance. Hologram materials such as silver halide sensitized gelatine [72], dichromated gelatine [73], photopolymer [74-76] and azobenzene polymer [77] have been used to fabricate the diffusers. The properties of source diffuser or mask and holographic medium have important effects on the diffuser.

As we discuss in the 3.1 section, ionic liquids can be used as additives to increase the sensitivity, the diffraction efficiency and the resolution of photopolymerizable holographic materials. Interestingly, there is strong dark diffusion of the monomers during the polymerization process. In this section, we described the applications of ionic liquids-photopolymerizable holographic materials in fabricating optic diffusers via lithographic writing process. A textured mask with random 2 – 15 μm apertures was used as the mask. The films of the materials were exposed to collimated UV light through the mask. Figure 10 illustrates the lithographic writing process. The film of ionic liquids-photopolymerizable holographic materials exposes to the UV light. During the exposure to the UV light, the monomers in the bright region were polymerized. Due to the reduction of the monomer concentration in the bright region, the monomers in the dark region diffuse to the bright region to form gradient structure with volume refractive index variation.

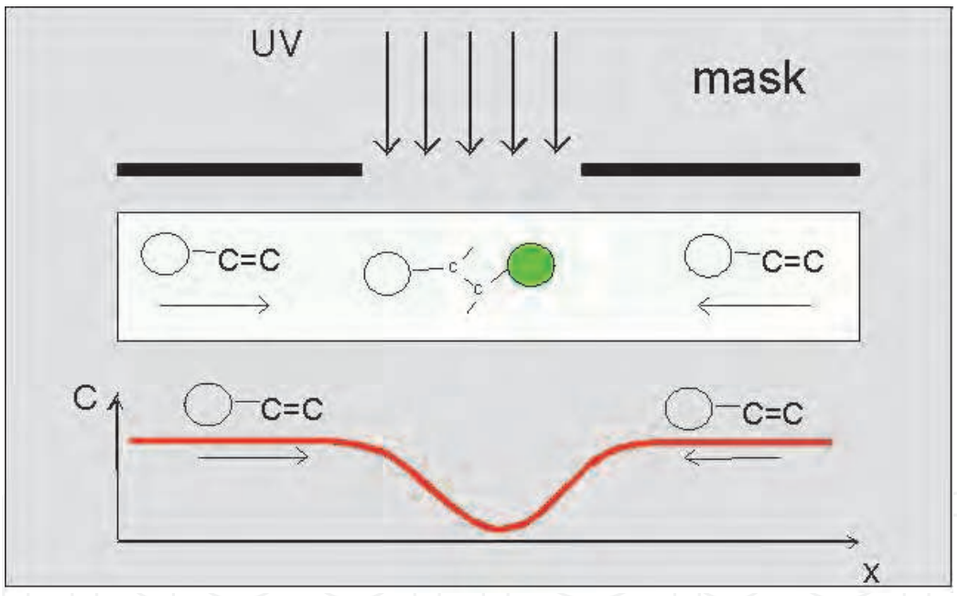

Fig. 10. Illustration of the lithographic writing process.

Symmetric and asymmetric diffusers with directional diffusion properties were both fabricating based on the ionic liquids-photopolymerizable holographic materials. For instance, using $BMIMBF_4$ as additive (sample 2, Table 1), the optic diffusers were obtained successfully with directional diffusion properties. The transmittance values varied from 7-57% within the measured angle (Figure 11a). In comparison, the composites without ionic liquids only afforded a transmittance film. Figure 11b, c show the photos of the diffusion patterns using 633 nm wavelength laser incident to the diffuser (a) a commercial particle-type diffuser and (b) the diffuser fabricated with sample 2. Comparing to the particle-type diffuser, our diffuser can scatter the light more uniformly and effectively.

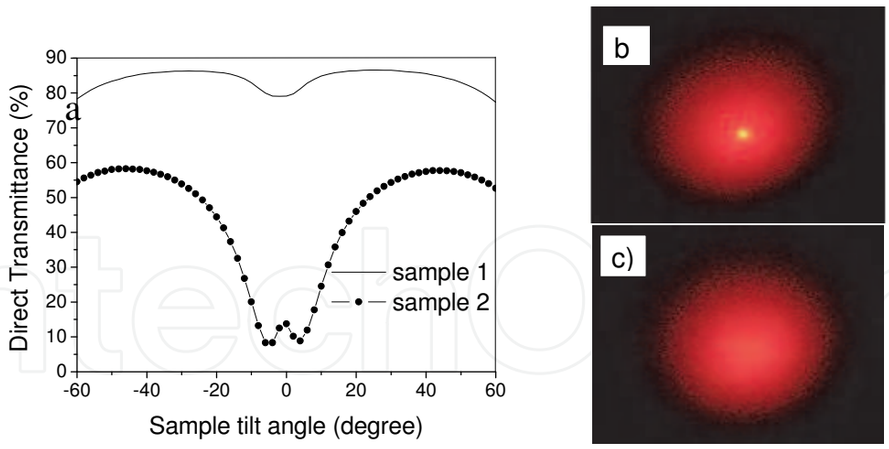

Fig. 11. a) The direct transmittance (%) versus the sample tilt angle (degree) of the symmetric diffuser. The different composites may be seen from the different symbol of the skeleton. Sample 1: PEGDMA, 4.0 g; Irg184, 0.2 g; Sample 2 : PEGDMA, 4.0g; $BMIMBF_4$, 1.0g; Irg184, 0.2 g. b) Photo of the diffusion pattern of the commercial particle-type diffuser. c) Photo of the diffusion pattern of the diffuser fabricated with sample 2.

The transmittance can be adjusted by changing the concentration of ionic liquids. Increasing the concentration of ionic liquids led to more haze as shown in Figure 12a. The materials can also be used to fabricate asymmetric diffusers. The films were exposed to a 60° angle to provide the asymmetric diffusers with directional diffusion property (Figure 12b). The characteristics of ionic liquids have an important influence on the diffusion properties of the diffusers. For instance, using 1-butyl-3-methyl-imidazolium hexafluorophosphate ($BMIMPF_6$) as additive (Table 1, sample 3), which only led to 4% diffraction efficiency in the thin hologram, however representing strong diffusion during the polymerization process. It led to a diffuser with a transmittance value variable from 50% to 79% within the measured angle. Although it had a high diffraction efficiency using polymerizable ionic liquids as additive (Table 1, sample 33, 34), it also led to a diffuser with bad diffusion properties.

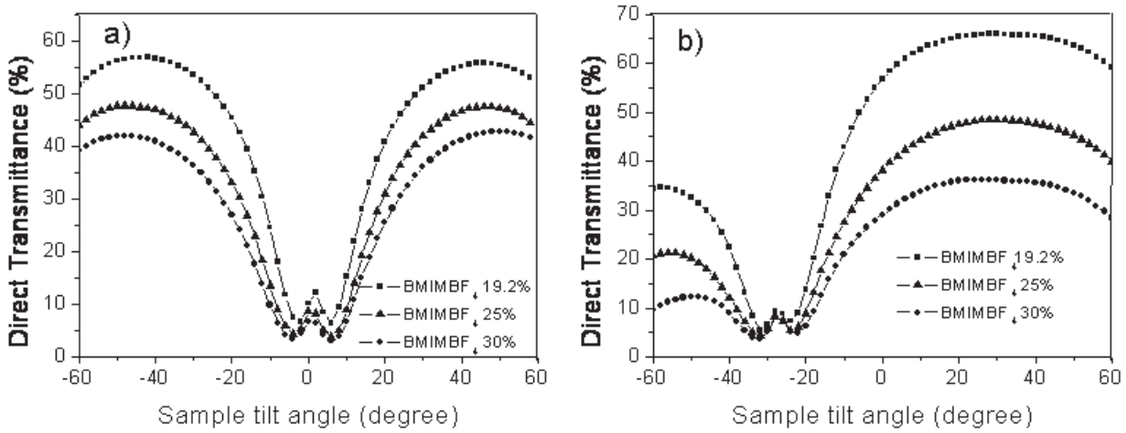

Fig. 12. The direct transmittance (%) versus the sample tilt angle (degree) of the symmetric diffuser. The different composites may be seen from the different symbol of the skeleton.

The cross section of the diffuser was examined with optical microscopy. The modulation of the refractive index was visible as shown in Figure 13 of the fiber structure. The surface of the diffuser was analysed with scanning electron microscopy (SEM). Figure 14 (a, b) shows the surface image of the diffuser based on sample 2. The pattern of the mask has been successfully recorded to form a surface-relief structure. Interestedly, there were many particles in a range tens to hundreds of nanometers on the surface, which possibly arise from phase separation of $BMIMBF_4$ in the bulk during polymerization. After that, we examined the cross section by SEM and found that most nanoparticles appeared in the region near both surfaces and that the bulk was more homogeneous [Figure 14 (c, d)]. The nanoparticles may function as particulate scatterers due to the low refractive index of n = 1.422 of $BMIMBF_4$, compared to n = 1.463 of PEGDMA.

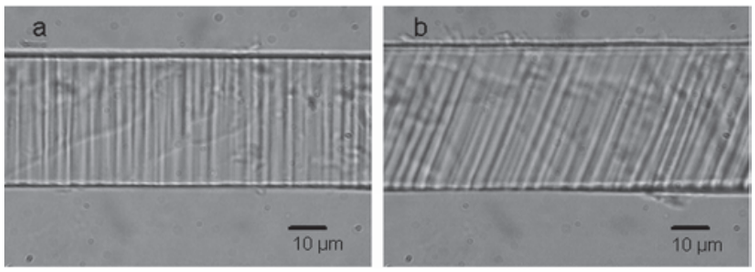

Fig. 13. The cross section optic images of the diffusers based on sample 2. (a) symmetric diffuser, (b) asymmetric diffuser.

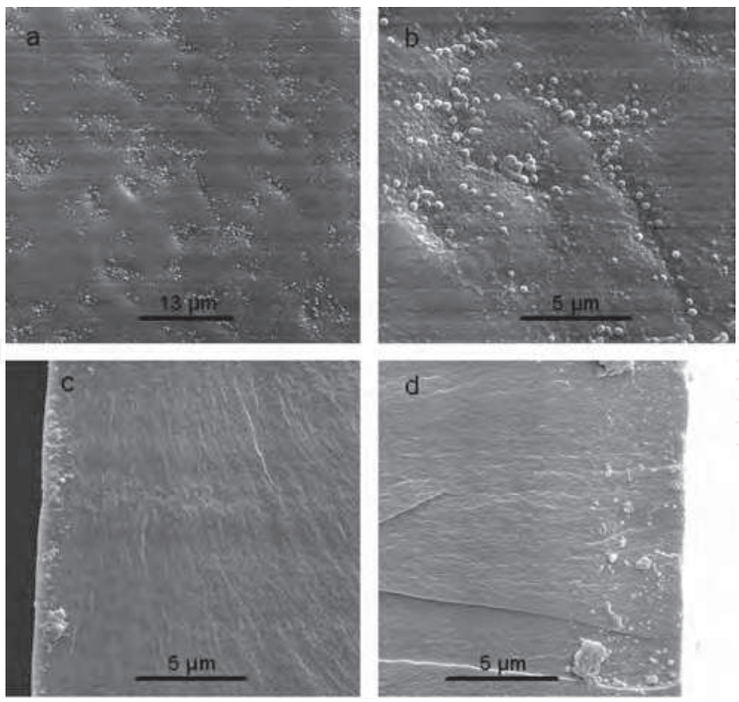

Fig. 14. The SEM images of the diffuser based on sample 2. (a) The surface image in 2000 × magnification. (b) The surface image in 6000 × magnification. (c) The cross section near the mask region. (d) The cross section near the substrate.

For comparison, the diffuser with bad diffusion properties was also observed with optic microscopy and scanning electron microscopy. The fiber structure was successfully formed, but there was no uniform phase separation during the polymerization process as shown the optic images and SEM images in Figure 15.

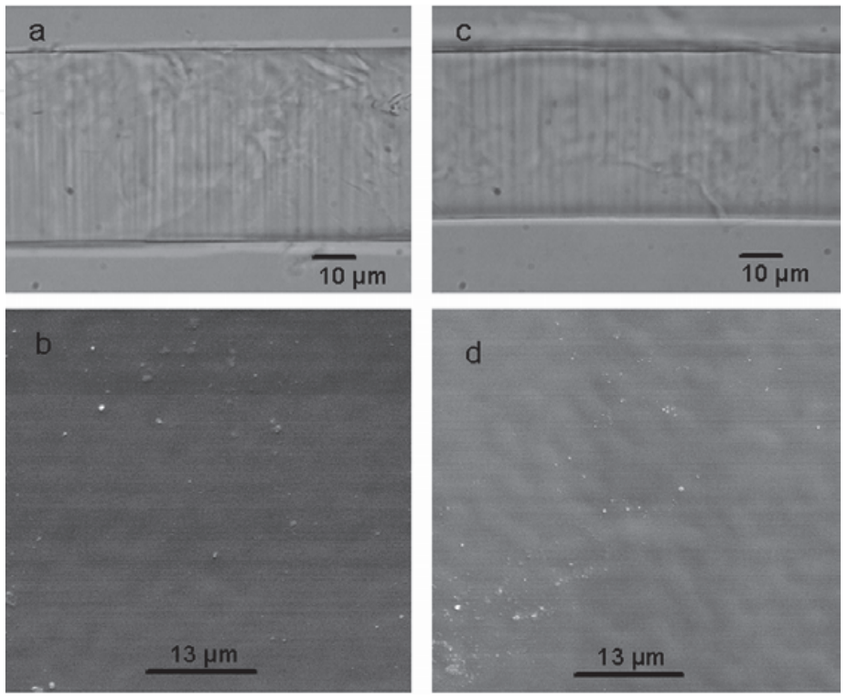

Fig. 15. a) The cross section optic images of the diffusers based on sample 3. b) The cross section optic images of the diffusers based on sample 19. (c) The SEM image in 2000 × magnification of the diffuser based on sample 3. (d) The SEM image in 2000 × magnification of the diffuser based on sample 19.

Most tested composites with ionic liquid as additive formed the fibre structure successfully, which indicates the volume refraction index variation. The diffusion-controlled polymerization in the presence of ionic liquid was beneficial for the formation of the fibre structure. Generally, during the lithographic process, the monomers in the bright region were polymerized. Due to the decreasing of the monomer concentration in the bright region, the monomers in the dark region diffuse to the bright region and polymerize to form the fibre structure. The properties of ionic liquids have an important effect on the diffuser. For instance, $BMIMBF_4$ afforded the better diffusion property than $BMIMPF_6$ and $BVIMBF_4$. One of the reasons is possibly due to the better formation of nanoparticles for the former. Thus, a forming mechanism for the diffuser with good diffusion properties can be proposed, which (during the exposure) leads to photopolymerization of the monomers in the immediate area exposed to ultra-violet light, accompanied and followed by diffusion of monomers from the unexposed regions into the exposed regions. By further polymerization the fibre structure is formed and a phase separation of ionic liquid is observed leading to the formation of nanoparticles. The fibre structure, the surface-relief structure and the formation of nanoparticles altogether are responsible for the directional diffusion property of the diffuser.

4. Conclusion

In summary, we investigated the influence of ionic liquids on photopolymerizable holographic materials. Although not all of the ionic liquids can be used as additives for photopolymerizable holograms, we found that imidazolium, pyridium and phosphonium based ionic liquids with proper counter anions, such as $BMIMBF_4$, $OMIMBF_4$, $BMIMNTf_2$, $BPMBF_4$, $OPMBF_4$, $OPMNTf_2$, Bu_4PBF_4, $C_{32}H_{68}PCl$ etc, can be used as additives to improve the properties of the materials. The sensitivity, resolution and the diffraction efficiency of the materials were increased efficiently. More interestingly, it presented strong dark diffusion of the monomers during polymerization process due to the diffusion controlled polymerization in the presence of some ionic liquids. Polymerizable ionic liquids were also used as additives in the holographic materials. High diffraction efficiencies were obtained as well. The photopolymerizable holographic materials have shown the potential application in fabricating optic diffuser for LCD. The symmetric and asymmetric diffusers with directional properties were successfully produced via lithographic recording method. The diffusion property can be regulated by changing the concentration of ionic liquid. The fiber structure, the surface-relief structure and the formation of nanoparticles lead to the directional diffusion property of the diffuser.

Ionic liquids are often named as so-called green solvents. However, "Greenness" of ionic liquids depends strongly on the structure. It is necessary to mention that ionic liquids exist as a component after the formation of the hologram. Low or no toxicity of ionic liquids is required for the actual application. Ionic liquids are designable. Our results are helpful for designing eco-friendly and successional holographic materials. Further researches on the application of ionic liquids in organic-inorganic nanocomposites and cationic ring-opening polymerization holographic materials are in progress.

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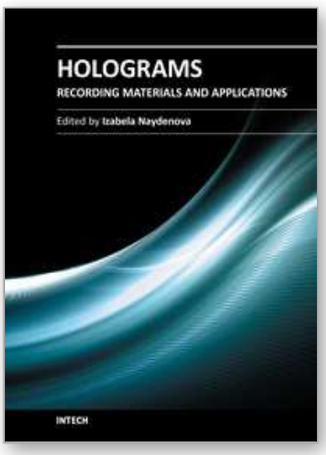

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Holograms - Recording Materials and Applications covers recent advances in the development of a broad range of holographic recording materials including ionic liquids in photopolymerisable materials, azo-dye containing materials, porous glass and polymer composites, amorphous chalcogenide films, Norland optical adhesive as holographic recording material and organic photochromic materials. In depth analysis of collinear holographic data storage and polychromatic reconstruction for volume holographic memory are included. Novel holographic devices, as well as application of holograms in security and signal processing are covered. Each chapter provides a comprehensive introduction to a specific topic, with a survey of developments to date.

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