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# Azobenzene-Containing Materials for Hologram

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## 1. Introduction

With the development of information technology, quick rate of data transfer and high capacity of data storage are expected for advanced recording media. Although data storage media and technique have been developed from soft discs, hard disk, CD-ROM and DVD-ROM to multi-layered blue-ray discs, undoubtedly, holography is one of the most fascinating and attractive techniques. As shown in Figure 1, which illustrates comparison of media in data storage and holographic ones. The optical holography is based on a three-dimensional storage method (Bieringer, 2000; Kogelnik, 1969). This provides unique opportunities for the next-generation storage technique by a simple recording and reading process.

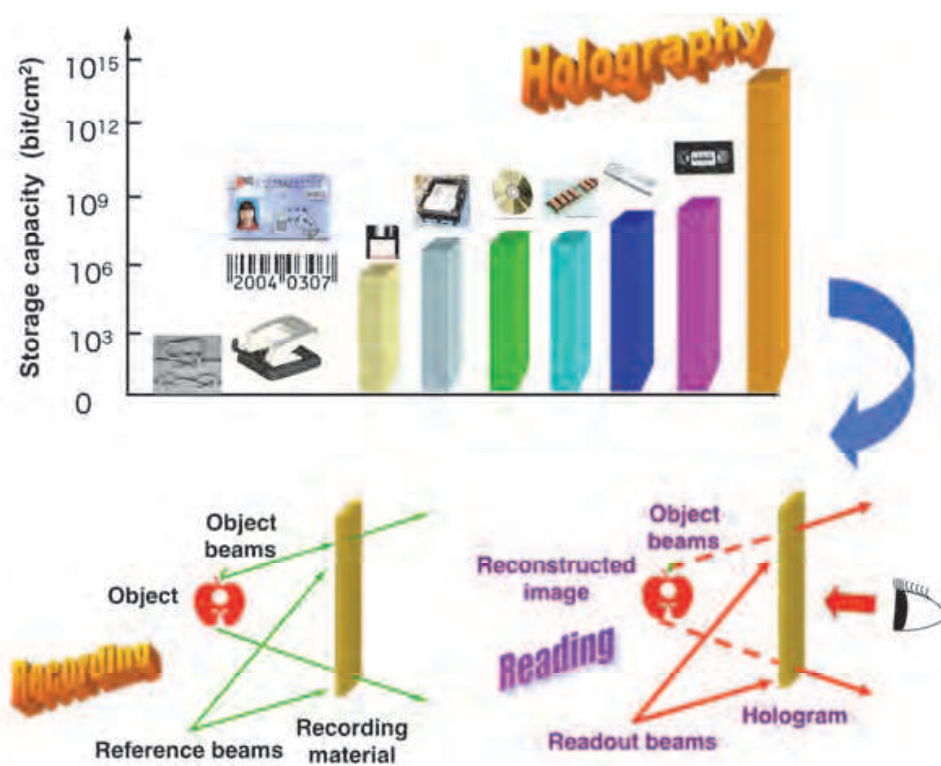


Fig. 1. Comparison of several data storage media (above) and scheme of holographic storage (below).

In 1948, Gabor first reported the holography method (Gabor, 1948), but this was not widely studied until the discovery of laser technique in 1960s (Kogelnik, 1969). The laser technology can easily supply two light beams with the same frequency and a stable phase difference for interference, which is necessary for recording information of one object (wavefronts, in Figure 2). Therefore, holography becomes to be a unique technique that enables simultaneous recording of both phases and amplitudes of light waves.

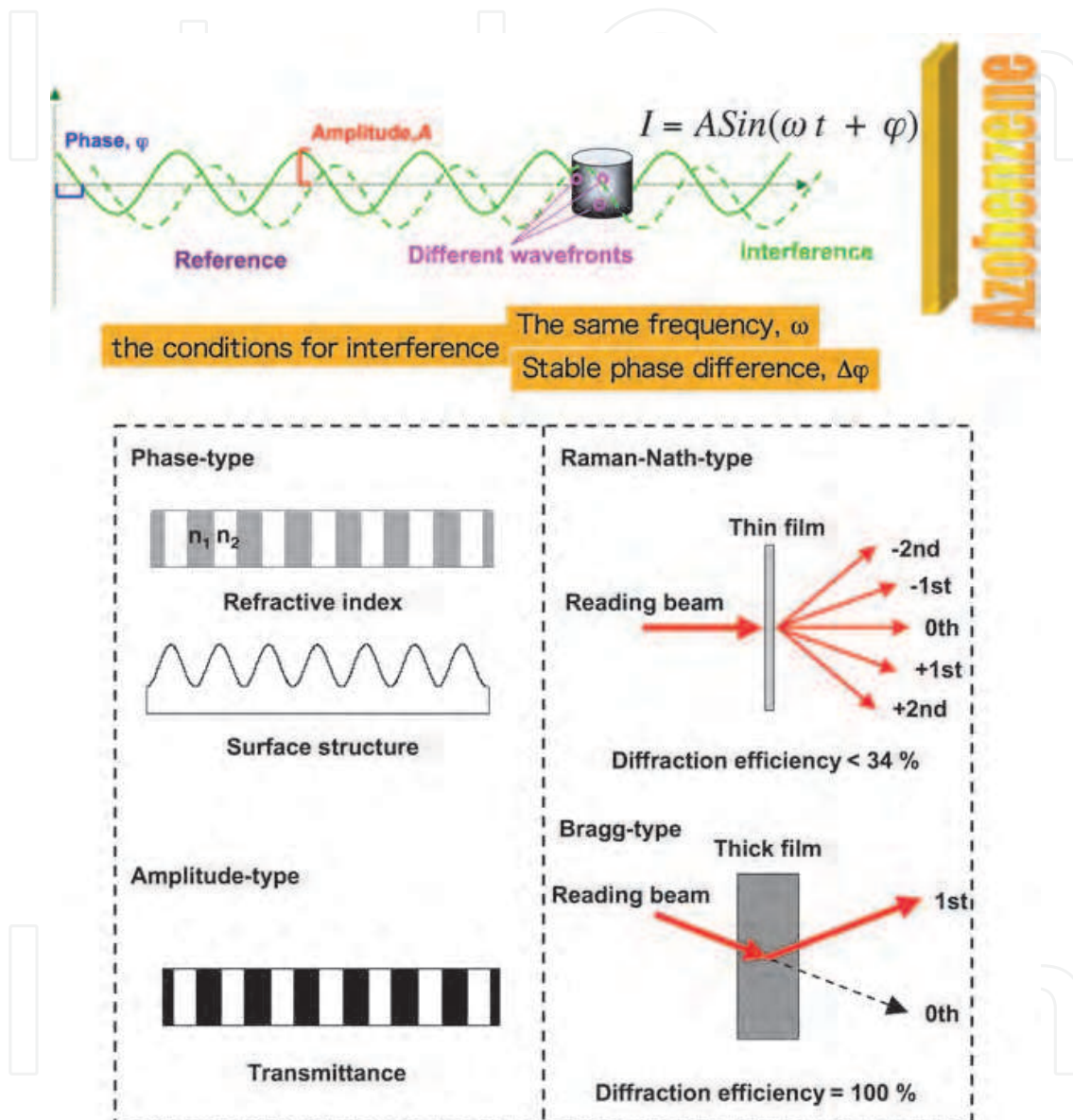


Fig. 2. Recording of one object (wavefronts) with interference of two coherent laser beams (above) and classification of holograms.

One of the most fascinating features of holography is that it is capable of recording and displaying a complete three-dimensional image of an object (a lot of wavefronts in Figure 2). In holography, recording the phase and amplitude of light waves are performed by periodic alternation of physical properties of materials. According to the manner of recording of interference patterns, holograms are mainly classified into two types (Collier, 1971; Smith, 1977). As shown in Figure 2, one is an amplitude-type hologram, in which the interference

pattern is recorded as a density variation in recording media. The other is a phase-type hologram, in which fringe patterns are recorded as a change in surface structure or refractive index. Theoretically, the diffraction efficiency of phase-type holograms is always higher than that of amplitude-type ones. Accordingly, the phase-type holograms for data recording are superior to the latter and most studies on holography are related to the phase-type ones. On the other hand, as shown in the bottom illustration of Figure 2, according to the thickness of recording films, the holograms can be categorized into Raman-Nath type (thin films) and Bragg type (thick films). The Raman-Nath hologram recorded in a thin film causes multiple diffraction of an incident beam, leading to low diffraction efficiency of the first diffraction beam with the maximum of about 34%. The Bragg hologram shows a single diffraction, which enables 100% diffraction efficiency.

Generally, storage media materials are among the most important for holographic applications (Smith, 1977). In the past two decades, much attention has been focused on the inorganic crystals as erasable holographic media. While organic materials offer incomparable advantages, such as simple processing, low cost and versatility. Desirable materials for holograms should exhibit high diffraction efficiency, fast response, high resolution, stable and reversible storage, low-energy consuming in the recording and reading processes as well as easy mass production. Therefore, introduction of organic materials is needed. Until now, none of them meets entirely the above-mentioned requirement, and absence of novel materials with high performance has become bottleneck of the holographic technique.

As one of the best known chromophores, azobenzene (AZ) with two benzene rings connected with an azo ( $-N=N-$ ) bridge in its chemical structures (Figure 3) has attracted much attention of materials chemists for their potential applications in holography. AZ-containing materials with photoresponsive functions can be easily modulated into hierarchical patterns by adjusting the input light properties - wavelength, intensity, polarization, phase, interference pattern, etc. As a result, holograms can be recorded in AZ-containing materials by photoinducing an orientation change of molecules in a periodic pattern obtained from interference of two coherent light beams, the object and the reference beams. Since photo-modulation of refractive index can be obtained in AZ-containing materials, the recorded hologram is phase-type. In this chapter, recent progress in AZ-containing liquid crystalline (LC) or amorphous polymers, polymer-dispersed low-molecular weight compounds or glassy oligomers will be discussed.

## 2. AZ-containing materials

An AZ moiety is well-known for its reversible photoisomerization, which may act as both a mesogen and a photoresponsive moiety when it is attached with soft substituents. Both photoisomerization and photoinduced LC-to-isotropic phase transition are involved in AZ-containing LC materials. A myriad of AZ derivatives can be tailored by modifying the substituents in the two benzene rings, resulting in their maximum absorption from the ultraviolet to visible regions. According to the electron-absorption properties, three kinds of AZ chromophores have been summarized as shown in Figure 3 (Natansohn & Rochon, 2002; Kumar & Neckers, 1989). The left side "AZ" has relatively poor  $\pi-\pi^*$  and  $n-\pi^*$  absorbance overlap and the lifetime of the cis-isomer is relatively long. The middle one is "amino-AZ", and there is significant overlap of the two bands and the cis-isomer lifetime is shorter. The right side AZ is "pseudostilbene", where the AZ is usually substituted with electron-donor and electron-acceptor substituents in both ends of the framework.

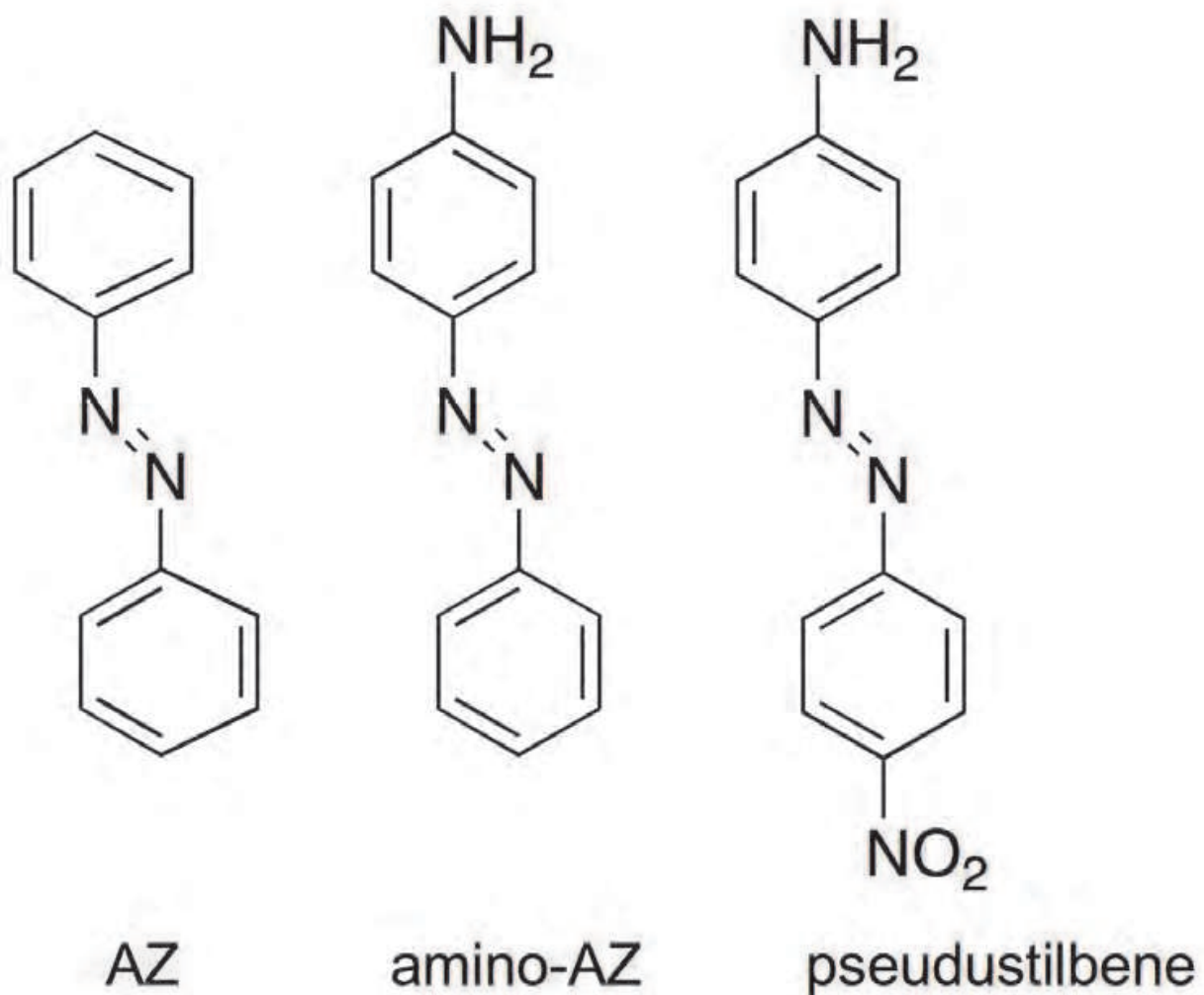


Fig. 3. Examples of three kinds of AZs classified by Natansohn and Kumar.

Generally, AZ-containing materials show several photoresponsive features like trans-to-cis photoisomerization, polarization-selective photoalignment, photochemical phase transition and photoinduced cooperative motions, as shown in Figure 4 (Yu & Kobayashi, 2010; Chen et al., 2010a). Upon UV irradiation, trans-to-cis photoisomerization often occurs for AZ-containing materials in solutions or solid states, leading to a large change in molecular shape and polarizability. The cis-isomers can return to their trans-isomers by thermal treatment or visible light irradiation. When a linearly polarized light is used, AZs selectively absorb light with the polarization direction parallel to their transition moments. The probability of the absorption is proportional to the  $\cos^2 \theta$  (Figure 4), where  $\theta$  is the angle between the transition moment of an AZ and the light polarization direction. Combining the polarization-selective trans-to-cis isomerization and un-selective back cis-to-trans isomerization, the number of AZ moieties with their transition moments normal to the light polarization direction gradually increases, resulting in the light-selective alignment, with transition moments of AZs almost perpendicular to the polarization direction of the actinic light. This is well known as the Weigert effect (Weigert, 1919). Such a photoalignment process is reversible, which means that AZs can be re-orientated to any controlled directions by choosing appropriate polarization direction of light (Yu & Ikeda, 2011).

When AZ-containing materials possess an LC phase, photoinduced phase transition can be caused in the LC phase since the trans-AZ can be a mesogen because its molecular shape is rod-like, whereas the cis-AZ never shows any LC phase due to its bent shape. When photoinert mesogens (like cyanobiphenyl groups) exist with dopant AZs, photoinduced molecular cooperative motion can be observed (Ikeda, 2003). If a small proportion of AZ molecules change their alignment in response to an external light stimulus, the other LC molecules also alter their alignment, coinciding with the ordered AZs pre-aligned. Actually, only a small amount of energy as to induce an alignment change of about 1 mole% of LC molecules is enough to bring about the alignment change of the whole system of AZ and LC mixtures. In other words, a huge amplification of light signals is possible in LC photonic systems owing to the molecular cooperative motion. As shown in Figure 4, both photoalignment and photochemical phase transition can be isothermally caused although the photoinert mesogens do not absorb the actinic light. These properties have been widely utilized in display, optical devices and holograms.

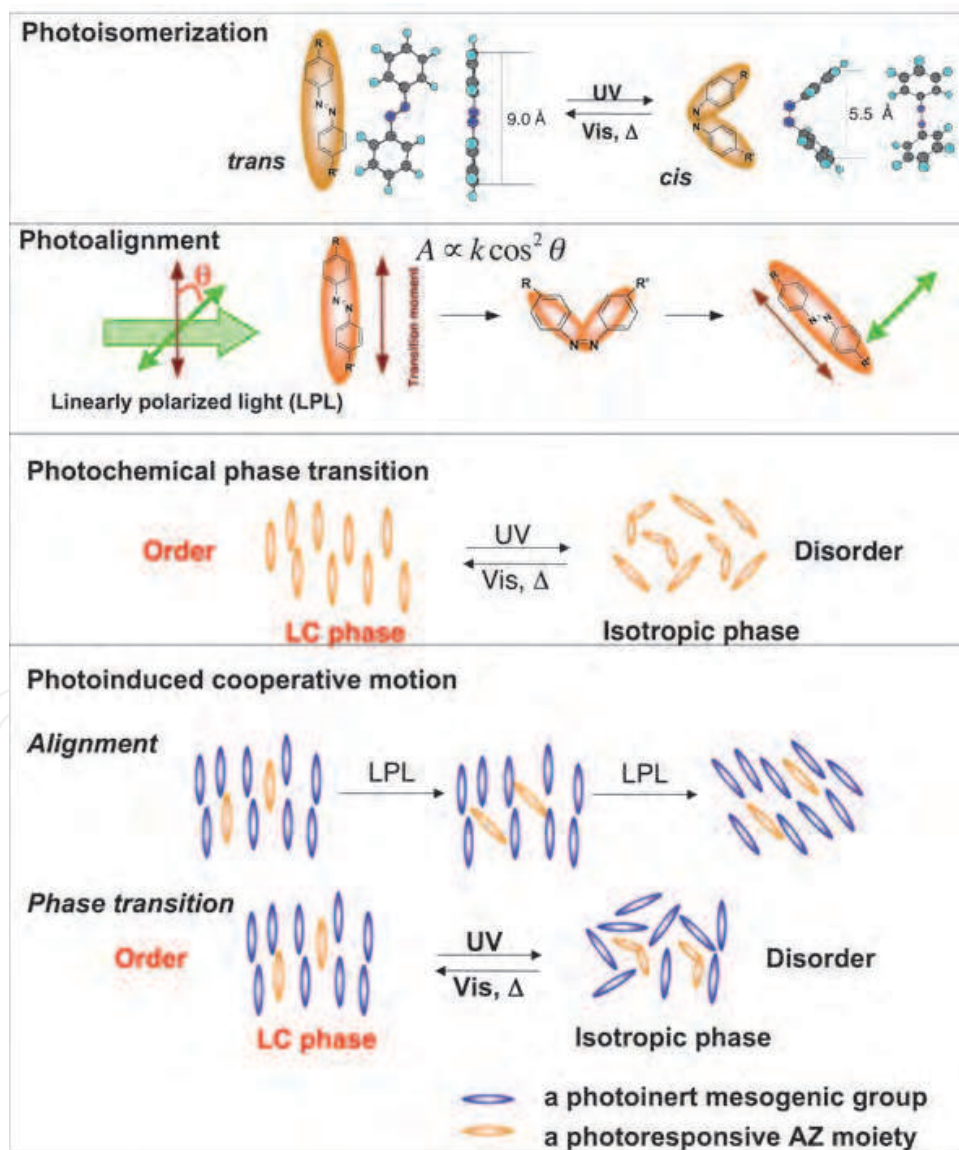


Fig. 4. Summarized properties of AZ-containing materials.

### 3. Low-molecular-weight AZs

Because of easy preparation and high purity of low-molecular-weight compounds, the application of AZ materials for recording holograms began with them. Formation of holographic gratings in films of poly(vinyl alcohol) doped with low-molecular-weight AZ compounds was first reported by utilizing photoisomerization of AZs (Todorov et al., 1983, 1984, 1985). The holographic gratings recorded in the polymer-based samples were self-developing and auto-erasing or re-writable since the thermally induced back isomerization of AZs could be easily obtained (Pham et al., 1997). To increase the formed birefringence  $|n_2 - n_1|$  shown in Figure 2 and enhance the performance of recorded holograms, polymer-dispersed AZ-containing low-molecular-weight LC compounds were also employed as recording media (Tondiglia et al., 1995). Due to the existence of low-molecular-weight LCs, the diffraction efficiency of the gratings could be electrically controlled (Sutherland et al., 1994). Moreover, dynamic holography was achieved in AZ-doped nematic LCs (Chen & Brady, 1993).

Although many research focused on the low-molecular-weight AZ-doped polymers, the stability of the induced anisotropy was low. To improve stability of the recorded gratings, molecular glasses fabricated with low-molecular-weight AZ compounds were developed (Shirota et al., 1998). This kind of materials can form stable amorphous and homogenous films without scattering of visible light (Nakano et al., 2002). Surface-relief gratings were successfully inscribed although the AZ derivatives were confined in the glassy states. More interestingly, low-molecular-weight AZ crystals and co-crystals also showed capability of formation of surface-relief gratings (Nakano et al., 2005). It was believed that photoreaction only occurred in the surface.

For holograms recorded in low-molecular-weight AZ materials, gain effect often occurs. It was reported that diffraction efficiency of gratings recorded in calamitic LC materials with low-molecular-weight compounds was increased sharply after annealing (Stracke et al., 1999). In recording holograms using pentaalkynylbenzene derivatives, a strong gain effect was obtained by the selective growth of crystals in the non-irradiated areas (Frese et al., 2003). For smectic trisazomelamine, the gain effect was acquired accompanied by the growth of surface modulation. At elevated temperatures, the free volume available to mesogens increased and the thermal movement led to a collective orientation along the direction given by those groups pre-aligned by the recording beams. This caused an increase of the order degree in the pre-orientated domain, which contributed to the increase of diffraction efficiency of holograms.

## 4. AZ-containing polymers

### 4.1 AZ-containing amorphous polymers

Low-molecular-weight AZ materials are superior in terms of mobility. However, it is often difficult to prepare holographic gratings with narrow fringe spacing (i.e., high resolution) and high stability because of the high mobility of AZ molecules with low molecular weight. From the application point of view, AZ-containing polymer materials might be one of the best choices for holograms because of their simple processability and high stability. On the other hand, the ordered structures or photoinduced alignment of chromophores can be easily fixed in polymer matrix.

In 1995, two groups independently reported surface-relief gratings inscribed in AZ-containing polymer materials almost at the same time (Rochon et al., 1995 ; Kim et al., 1995).

In films of poly[4'-(2-acryloxy)ethylamino-4-nitroazobenzene] (pDR1A, Figure 5a), surface-relief gratings with a sinusoidal shape was recorded with an interference pattern of two light beams at 514 nm. The obtained grating structures were stable but could be erased by heating the polymer above its glass transition temperature. In addition, no permanent damage of the film was observed. Multiple gratings can be simultaneously written and gratings can be overwritten (Rochon et al., 1995). Using an epoxy-based amorphous polymer containing AZ side groups (Figure 5b), surface-relief gratings with relatively large amplitude was successfully inscribed with two laser beams at 488 nm. Furthermore, recording perpendicular gratings on the same film was also achieved. Such surface-relief gratings in amorphous polymer films showed uniform and controllable morphologies, like the depth of relief, the grating periodicity, and so on. Moreover, more complicated topological surfaces were tailored by superimposing several surface-relief gratings. Recently, the recorded surface-relief structures were studied for potential applications as LC alignment (Li et al., 1999), polarization discriminator, waveguide couplers (Viswanathan et al., 1999) and antireflective coatings (Natansohn & Rochon, 2002).

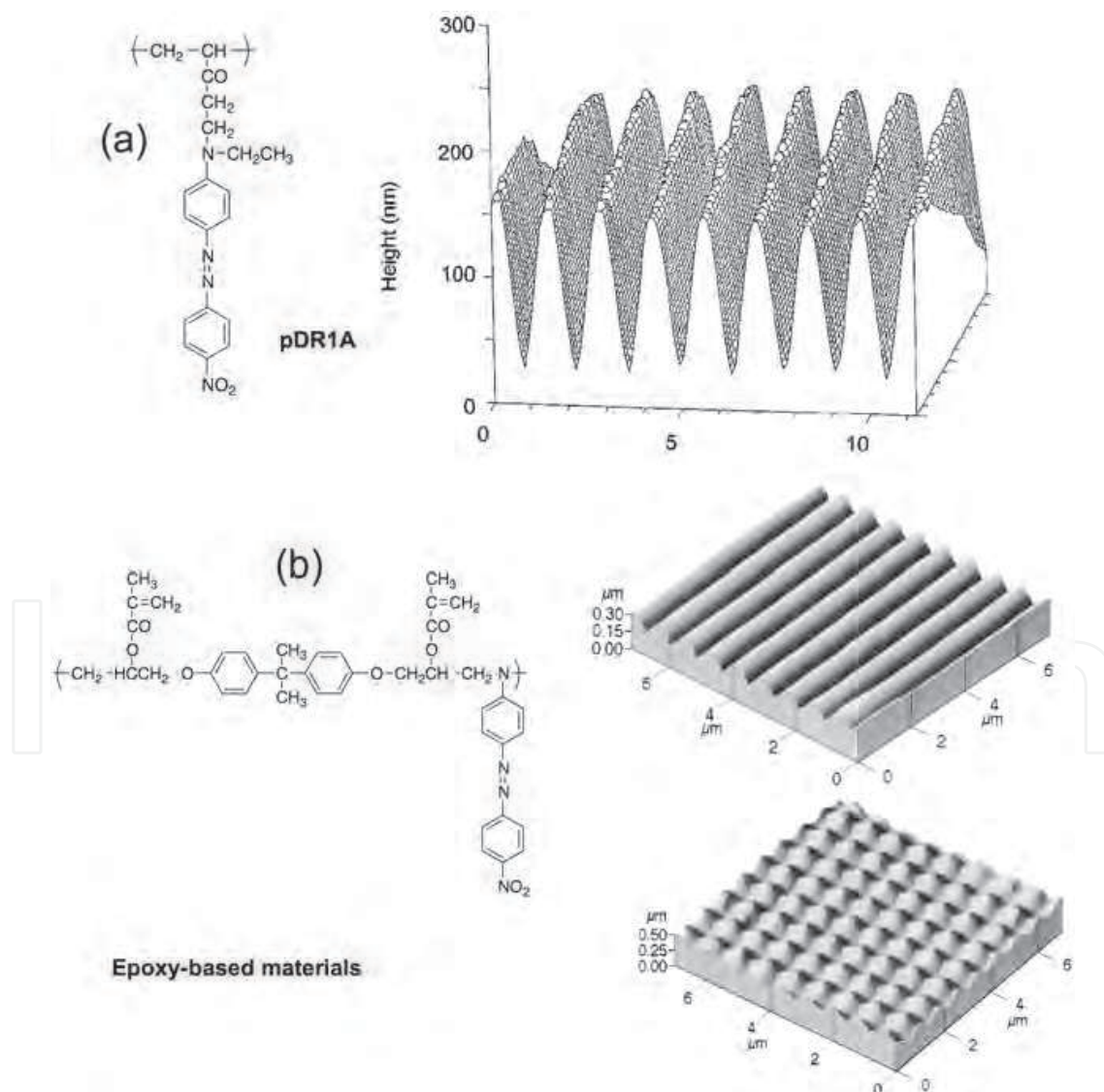


Fig. 5. Surface-relief gratings recorded in AZ-containing amorphous polymer materials.



## 4.2 AZ-containing LC polymers

Comparing with amorphous materials, LC materials possess unique features like self-organization, fluidity with long-range order, molecular cooperative motion, formed large birefringence and anisotropy in various physical properties (optical, mechanical, electrical and magnetic), and alignment change induced by external fields at surfaces and interfaces (Ikeda, 2003; Yu & Kobayashi, 2010). Therefore, LC materials can bring about a larger change in refractive index relative to amorphous ones. An alignment change of LC materials in a periodic fashion can be easily induced upon irradiation with interference patterns by overlapping two coherent beams, resulting in a large refractive-index modulation. This can contribute to a high diffraction efficiency of recorded gratings. In films of AZ-containing LC polymers, both surface-relief and refractive-index gratings can be recorded correspondingly.

Wendorff et al. showed that holographic gratings could be inscribed in LC polymers composed of AZ moieties and photoinert mesogenic groups (Eich et al., 1987; Eich & Wendorff, 1987; Anderle & Wendorff, 1994). Hvilsted et al. achieved holographic gratings with diffraction efficiencies of about 40% in AZ-containing LC polyesters (Hvilsted et al., 1995). Recently, formation of holographic gratings in side-chain LC polymers containing AZ moieties by means of photochemical phase transition was intensively studied. Hasegawa et al. achieved dynamic holographic gratings by means of photochemical nematic-to-isotropic phase transition in LC copolymers containing an AZ moiety with strong donor-acceptor substituents in side chain (pseudostilbene-type AZs in Figure 3). As shown in Figure 6, the inscription and removal of holographic gratings with a narrow fringe spacing of 1.4  $\mu\text{m}$  was obtained within 150 and 190 ms, respectively (Hasegawa et al., 1999a, 1999b). Moreover, the optical switching behaviors of the holographic diffraction were observed repeatedly by turning the writing beams on and off. Using a siloxane group as a spacer in preparation of LC polymers decreased the glass transition temperature of the designed materials. This was because of the flexibility of the siloxane unit, which resulted in an effectively photoinduced nematic-to-isotropic phase transition at room temperature and formation of real-time holographic gratings (Hasegawa et al., 1999c).

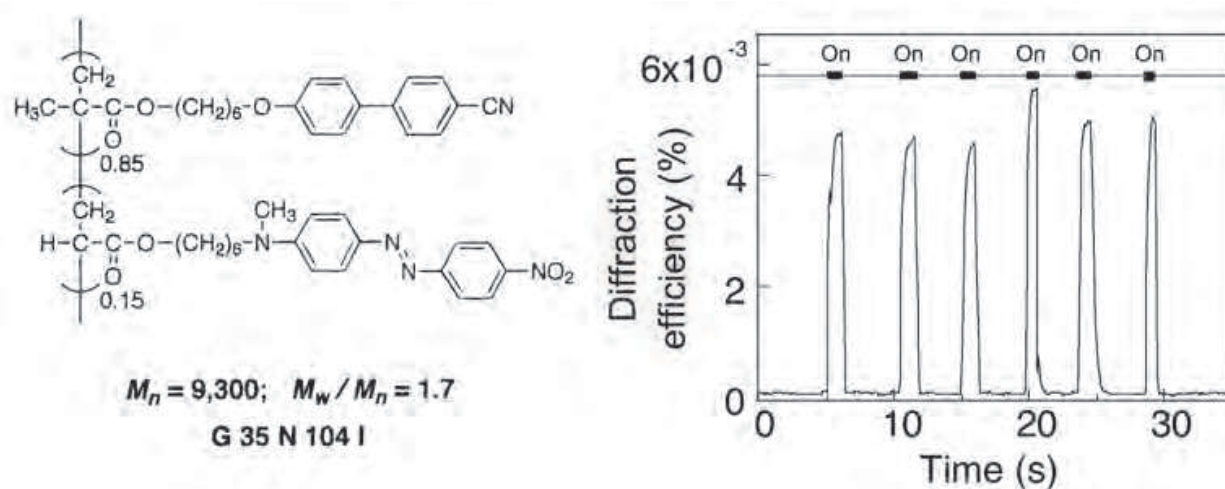


Fig. 6. Dynamic holographic gratings by means of photochemical phase transition in AZ-containing LC polymers.

In a nematic LC polymer with AZs as side mesogens, both surface relief and refractive index modulations were recorded, as shown in Figure 7. In nematic LC phase, the obtained gratings exhibited a higher diffraction efficiency than that recorded in the glassy state even though the amplitude of surface-relief structures of the former was lower than that of the latter one (Yamamoto et al., 1999). These indicated that the contribution of refractive-index gratings to the diffraction efficiency was larger than that of surface-relief gratings. Based on the same materials, holographic image storage using a photomask as an object was successfully obtained (Yamamoto et al., 2000).

To enhance the refractive-index modulation, both cyanobiphenyl and tolane groups were used as photoinert moieties to prepare LC copolymers with AZs as photoresponsive mesogens (Yoneyama et al., 2001, 2002). However, the photoresponse was not high enough due to a low content of AZ moieties in the copolymers. To improve the photosensitivity and induce a larger birefringence for holographic applications, a concept of molecular architecture of AZ-containing LC materials was proposed in Figure 8 (Okano et al., 2005). A tolane group was directly attached onto the 4- or 4'- position of AZ molecules to prepare an azotolane mesogen, which shows far longer molecular conjugation length than one single tolane group or an AZ moiety (Okano et al., 2005). Figure 8 lists the molecular structures and LC phase behaviors of a series of azotolane nematic LC polymers synthesized based on this principle, in which three, four and five benzene rings are included in the mesogens, respectively. All the prepared azotolane-containing LCPs showed a wide nematic LC range and exhibited a phase transition temperature higher than 200 °C (Okano et al., 2006). Obviously, the photoresponse of the designed LC polymer with high birefringence was greatly enhanced because of high density of AZ mesogens, resulting in formation of holographic grating in thin films within short time under low-intensity irradiation of recording beams.

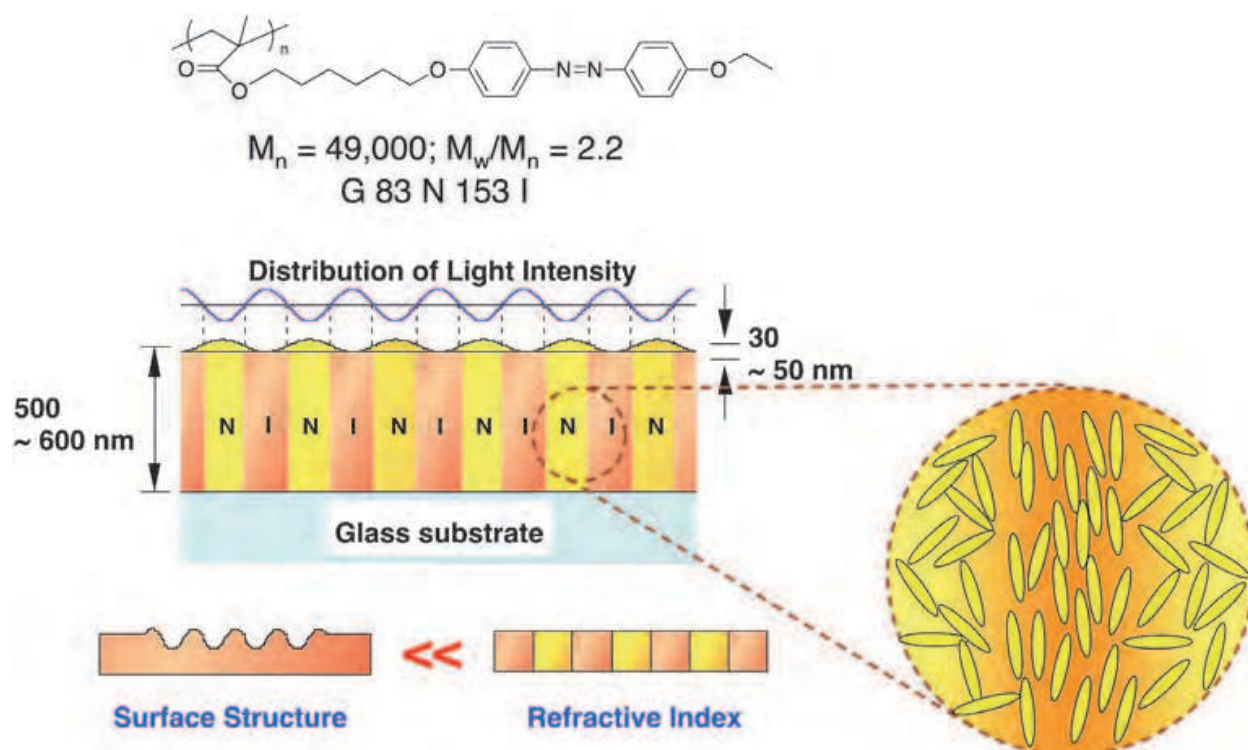


Fig. 7. Holographic gratings recorded in nematic LC polymer with AZs as side mesogens.

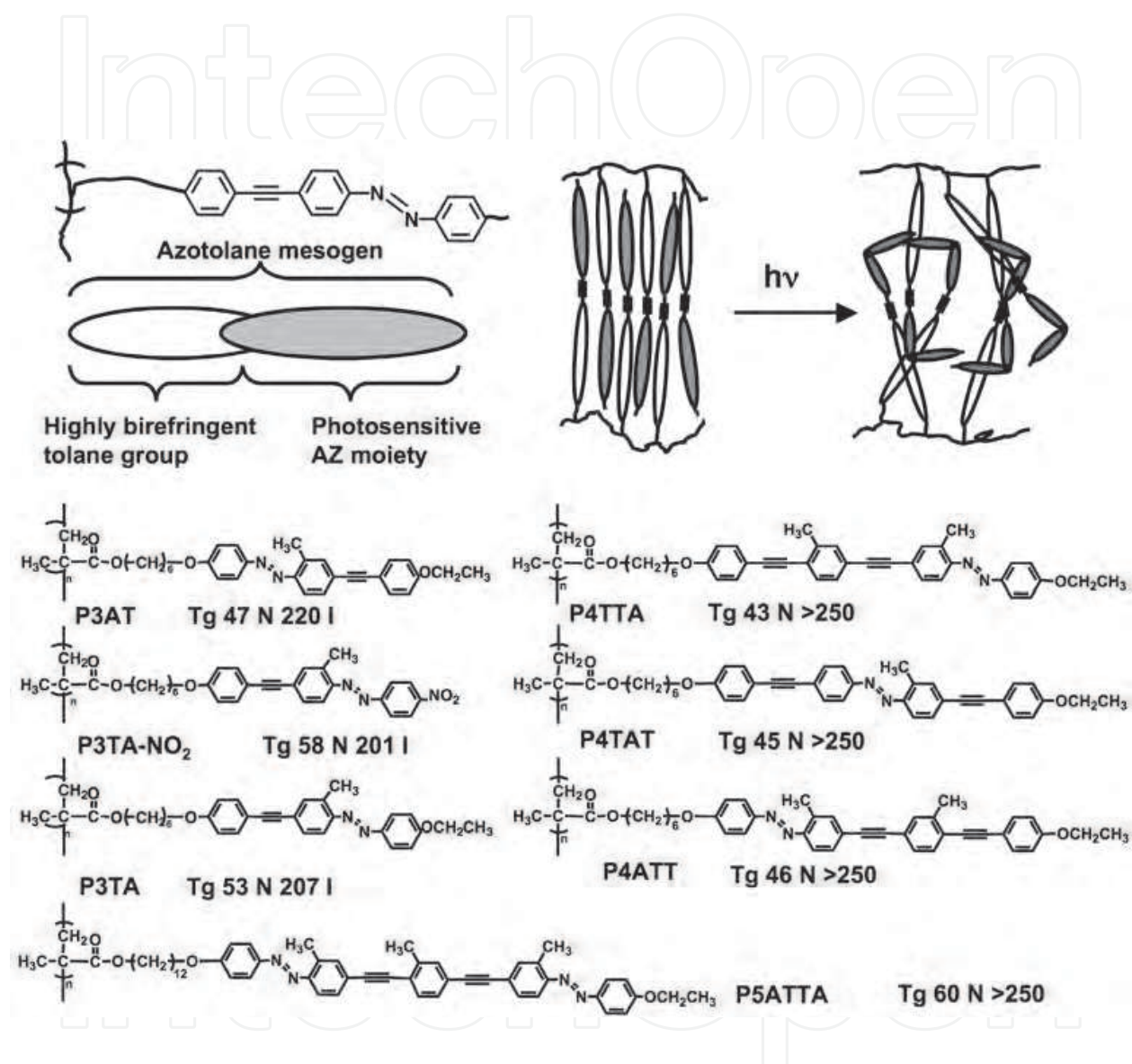


Fig. 8. Azotolane LC polymers with high birefringence for holograms.

Using two phase-type gratings recorded in LC cells (Figure 9), grating waveguide couplers with a flat surface were fabricated as shown in Figure 9 (Bang et al., 2007). When a probe beam at 633 nm was incident to one grating, the beam propagated in the waveguide and an output beam came out from the other grating with the throughput coupling efficiency of about 5%. Upon irradiation of the film between the two gratings with UV light to cause trans-cis photoisomerization and order-disorder transition of the AZ moiety, the intensity of the output beam was repeatedly switched upon alternating irradiation of visible light. It was found that the alternating irradiation at 366 and 436 nm induced reversible changes in the intensity of the output beam.

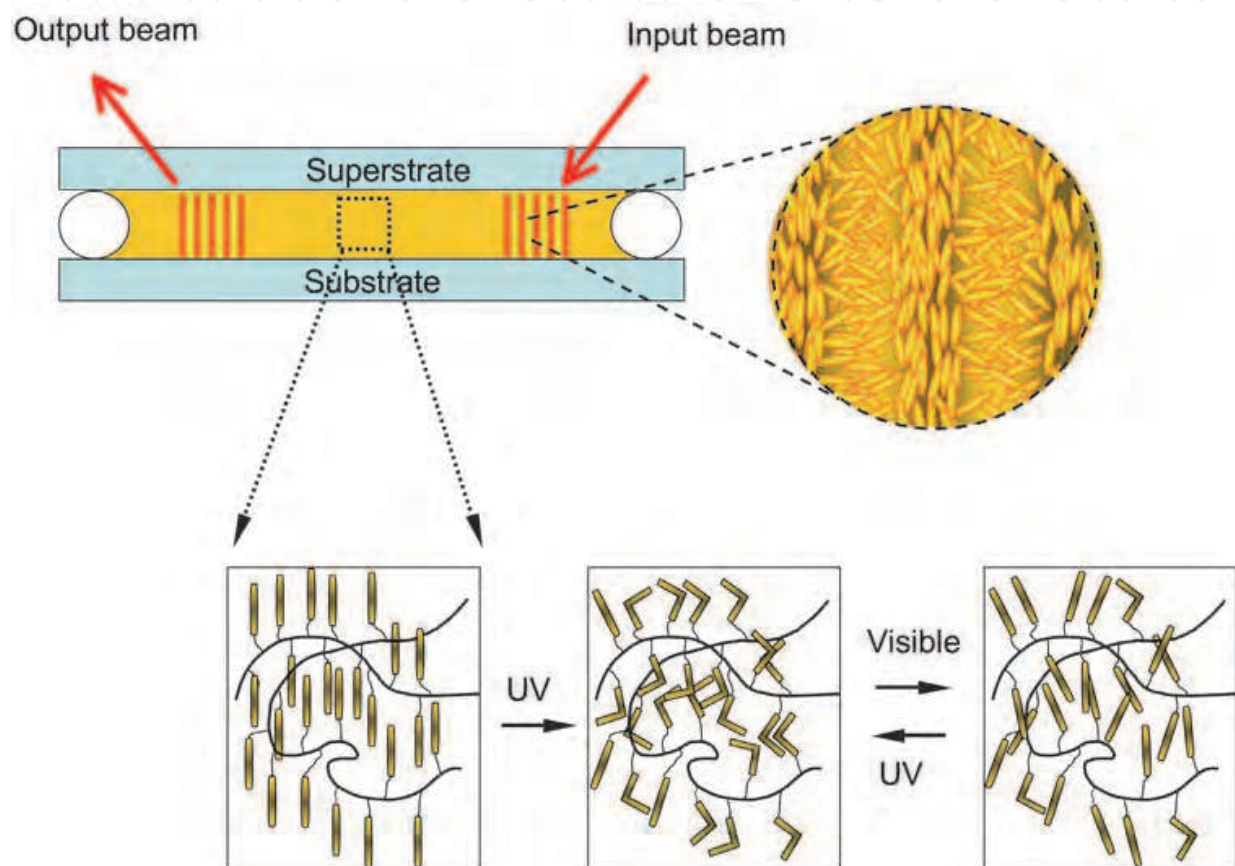


Fig. 9. Periodically flat-structured grating waveguide couplers and photo-switching behaviors.

Due to molecular cooperative motion of mesogens in LC polymers, it is difficult to record holographic gratings with a narrow periodicity in a subwavelength scale (Yu et al., 2008a). Pre-treatment with UV irradiation to induce cis-azobenzene-rich isotropic phase can illuminate such molecular cooperative effect of mesogens and enhance the photoresponse in an a lowly viscous state. These enabled us to obtain the subwavelength modulation of surface relief and refractive index with interference patterns in Figure 10 (Yu et al., 2008a). The surface relief of less than 10 nm and the refractive-index modulation were detected by atomic force microscopy in tapping and phase modes, respectively. A large phase retardation and formed birefringence were observed in the recorded subwavelength gratings.

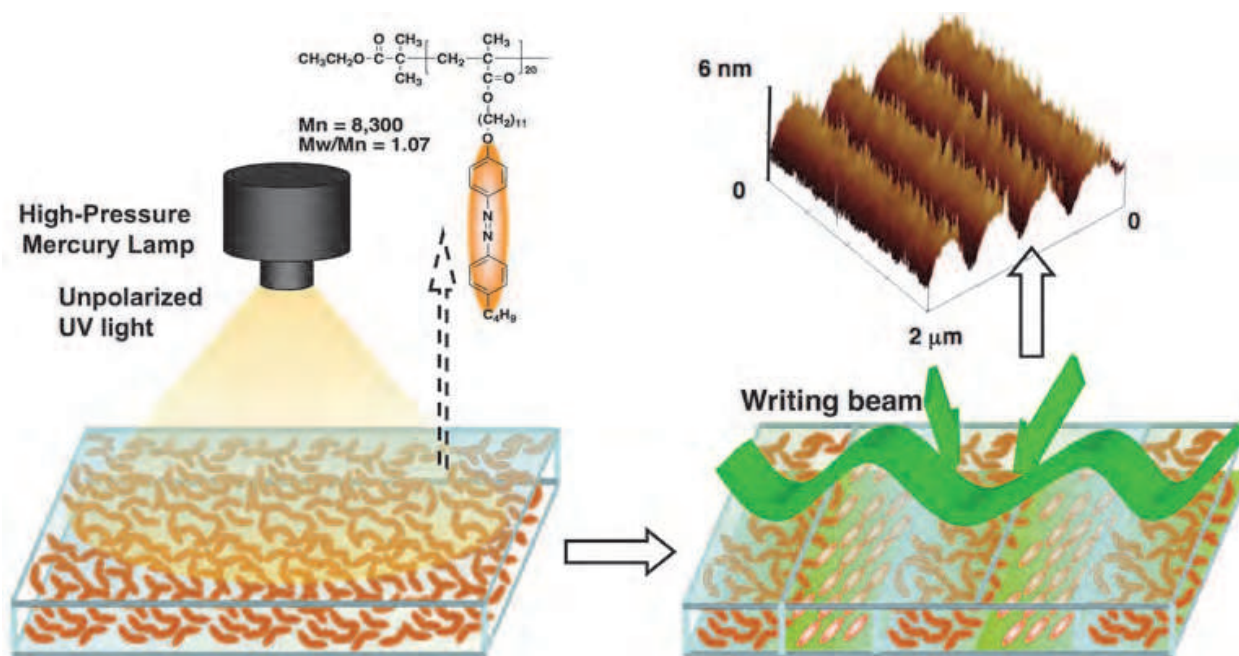


Fig. 10. Subwavelength modulation of surface relief and refractive index in LC polymer films.

#### 4.3 AZ-containing LC block polymers with well-defined structures

In LC block copolymers with well-defined structures, microphase separation often occurs because of the inherent immiscibility of the different blocks, resulting in diverse nanostructures like nanospheres and nanocylinders (Yu et al., 2006a, 2006b, 2007d, 2007e, 2009b, 2011; Chen et al., 2010b). Generally, the phase-segregated nano domains are far smaller than the wavelength of the visible light (Yu et al., 2007b, 2007c), making it possible to get rid of the scattering effect. Such kinds of AZ-containing LC block polymers with nanoscale phase separation have been regarded as one of ideal materials candidates for holograms.

Generally, the diffraction efficiency is one of the most important parameters for holographic gratings. In amorphous polymer materials, a surface-relief grating contributes mainly to diffraction efficiency. Recently, microphase separation of AZ-containing LC block copolymers was used to control diffraction efficiency by enhancement of surface relief upon thermal annealing (Yu et al., 2005a, 2009a; Naka et al., 2009). As shown in Figure 11, both surface-relief and refractive-index gratings were recorded upon irradiation of an interference pattern, in which selective photoisomerization and the isotropic-to-LC phase transition were induced in the bright areas of pre-treated films. The diffraction efficiency of the gratings depended strongly on the polarization of the reading beam because of the photoalignment of mesogens in the bright area of the writing patterns. After grating formation, the surface-relief structures with a sinusoidal shape were clearly observed in the AFM images (Figure 11). The fringe spacing of the surface relief was  $2.0 \mu\text{m}$ , which was identical to that of the refractive-index gratings. Then nanoscaled microphase separation was proceeded by annealing the grating sample. As a result, the surface relief was increased to about  $110 \text{ nm}$  (18.3 % of the film thickness), almost one order of magnitude larger than that before annealing. The peak-to-valley contrast became more explicit after annealing, due to the enhancement of the surface modulation. Furthermore, the sinusoidal shape of the surface profile became a little irregular, indicating that the LC alignment was disturbed upon microphase separation. Together with the enhancement of surface relief,

the diffraction efficiency increased to about 9.0 %, almost two orders of magnitude larger than the diffraction efficiency before annealing. This increased diffraction efficiency might be ascribed mainly to the enhancement of surface modulation. Furthermore, multi-processes of the refractive-index gratings were successfully achieved as presented in Figure 11. The obtained grating structures were clearly observed in the polarizing optical microscopic pictures, which were also verified by their diffraction patterns (Yu et al., 2007a).

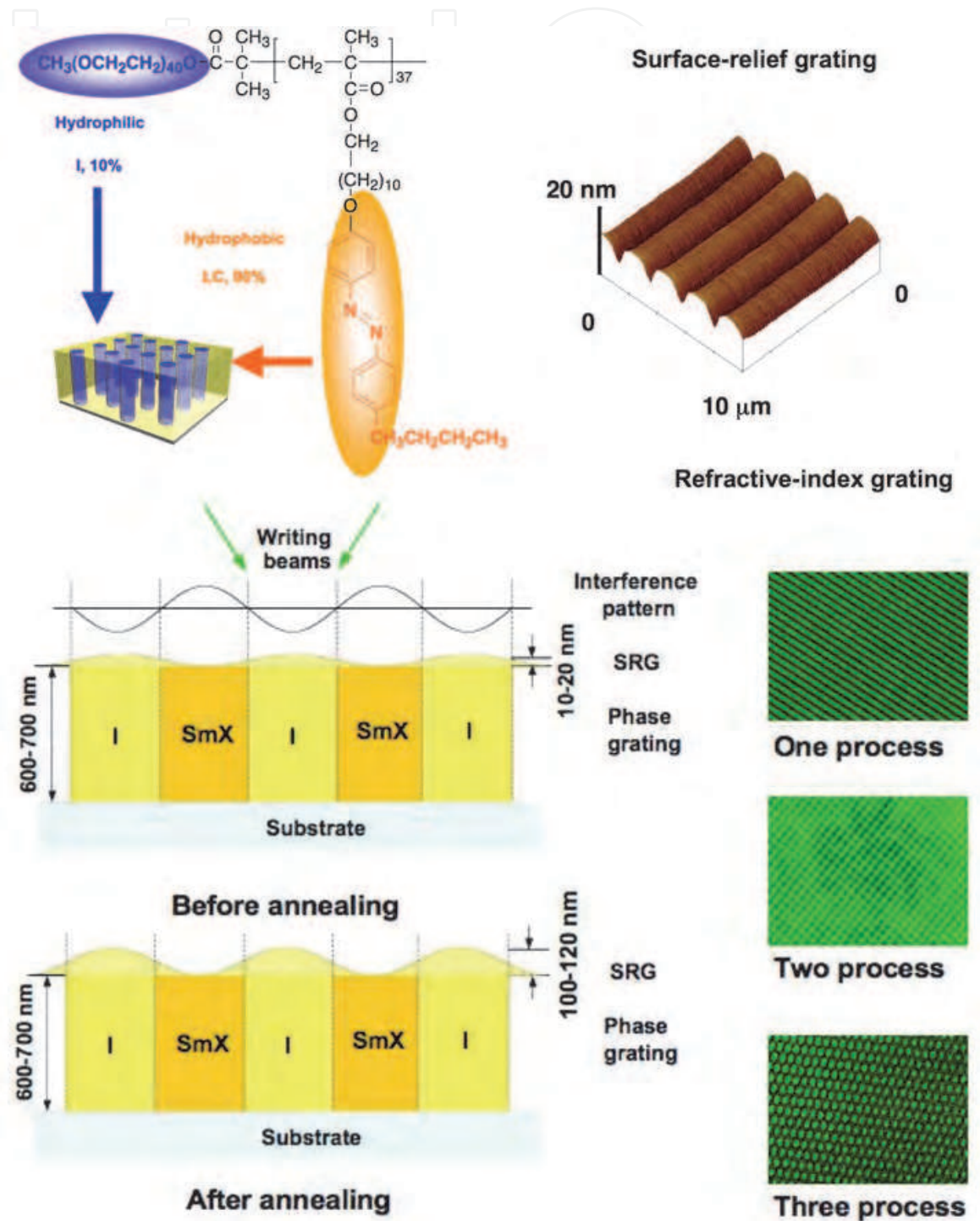


Fig. 11. Holographic gratings recorded in AZ-containing LC block copolymers with well-defined structures and enhancement of gratings upon microphase separation.

Comparing to other methods to control diffraction efficiency, such as gain effects, mechanical stretch, electrical switch, self-assembly, mixture with LC and cross-linking, the microphase-separation method had advantages of being simple and convenient (Yu et al., 2005a, 2009a). To precisely control diffraction efficiency of recorded gratings in the amphiphilic block copolymers, the effect of recording time on grating formation and enhancement was systematically studied. The best enhancement effect was obtained at 10 s recording upon microphase separation. By adjusting the recording time, the diffraction efficiency was finely controlled from 0.13% to about 10% (Yu et al., 2009a).

As described in section 2, a small external stimulus can induce a large change in refractive index of the materials by the cooperative effect between photoresponsive AZ moieties and photoinert groups. These properties have been widely used in holographic recording, which is especially useful in AZ-containing block copolymers with mesogens in the minority phase dispersed in glassy substrates (Yu et al., 2007b). It was reported that the photoinduced mass transfer was greatly prohibited due to the microphase separation in grating recording, lack of surface-relief structures was observed (Breiner et al., 2007). Thus, refractive-index modulation plays an important role in the grating formation in such well-defined block copolymers.

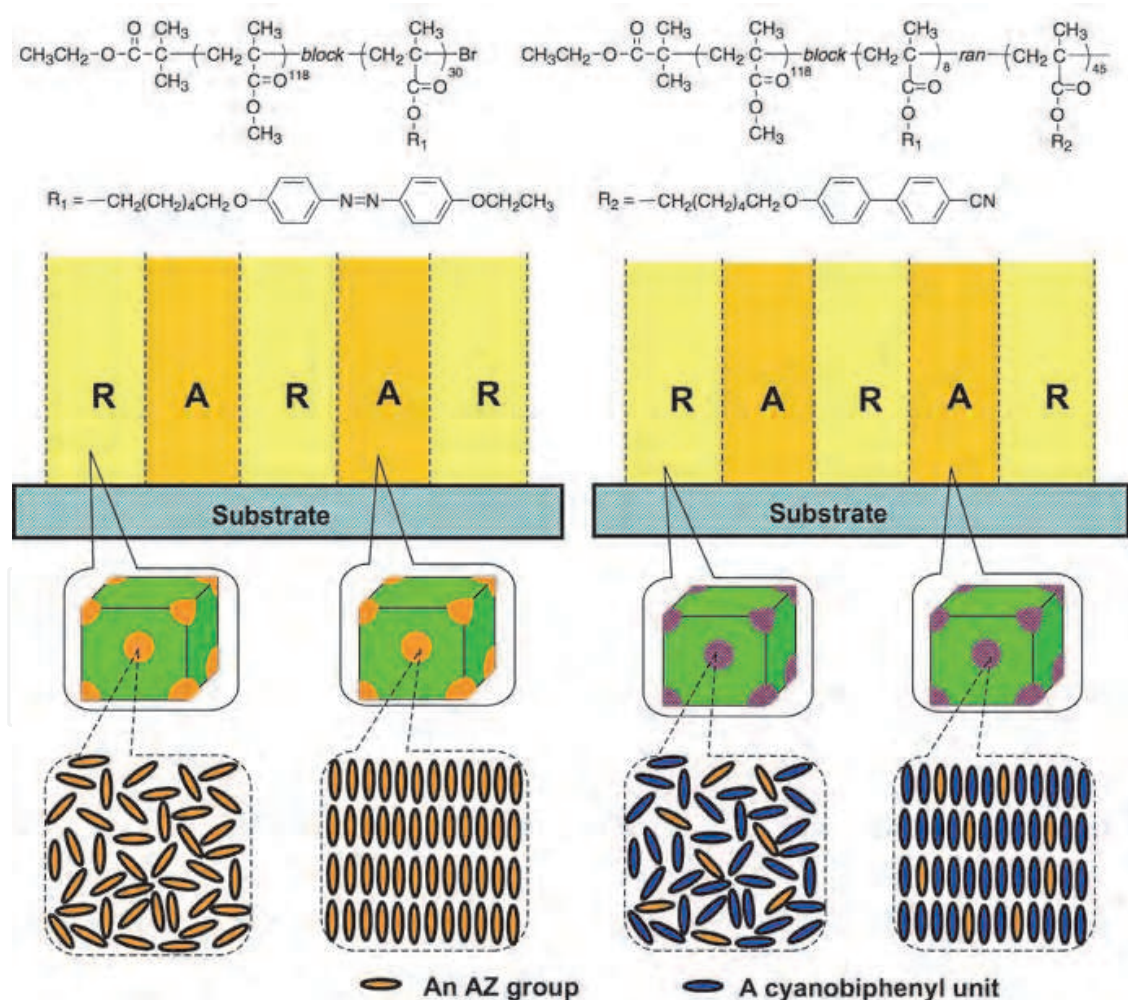


Fig. 12. Enhancement of surface-index modulation and prohibition of surface-relief gratings in block copolymers with photoresponsive AZ groups in the minority phase. (A, aligned, R, random).

As shown in Figure 12, holographic gratings were recorded in films of two polymethyl methacrylate (PMMA)-based block copolymers containing AZ moieties (Yu et al, 2008b). One was a well-defined diblock copolymer, and the other sample was a diblock random copolymer. Here, the diblock random copolymer consisted of two blocks, in which one segment was PMMA and the other mesogenic block was statistically random distributed. After grating formation, both films showed no formation of surface-relief gratings, and only refractive-index gratings were obtained. Upon irradiation of two coherent laser beams, refractive-index gratings in the diblock copolymer containing AZs were recorded by photoalignment of AZs dispersed in phase-separated domains. In contrast, the photoalignment of the AZ moieties was amplified by the photoinert cyanobiphenyl moieties as a result of the cooperative effect in the diblock random copolymer. This led to a similar refractive-index modulation, although the AZ content was lower in the diblock random copolymer. The cooperative motion was confined within the nanoscale phase domains, unlike the case of random copolymers with statistically molecular structures.

Being one of commercially available products, an ABA-type triblock copolymer, polystyrene (PS)-*b*-polybutadiene-*b*-PS, is famous for its thermoplastics. The hard block of PS with a content of 20-30 wt% forms the minority phase upon microphase separation, which acts as physical crosslinks for the majority phase of the soft block of rubbery polybutadiene (PB). Mechanical stretching can induce a large elastic deformation with recoverable properties. By applying this concept, block copolymers with thermoplastics were prepared (Bai & Zhao, 2001, 2002; Zhao et al., 2002). Upon stretching-induced elastic deformation of grating samples recorded in the thermoplastic block copolymers, fringe spacing or grating periodicity was successfully adjusted, as shown in Figure 13.

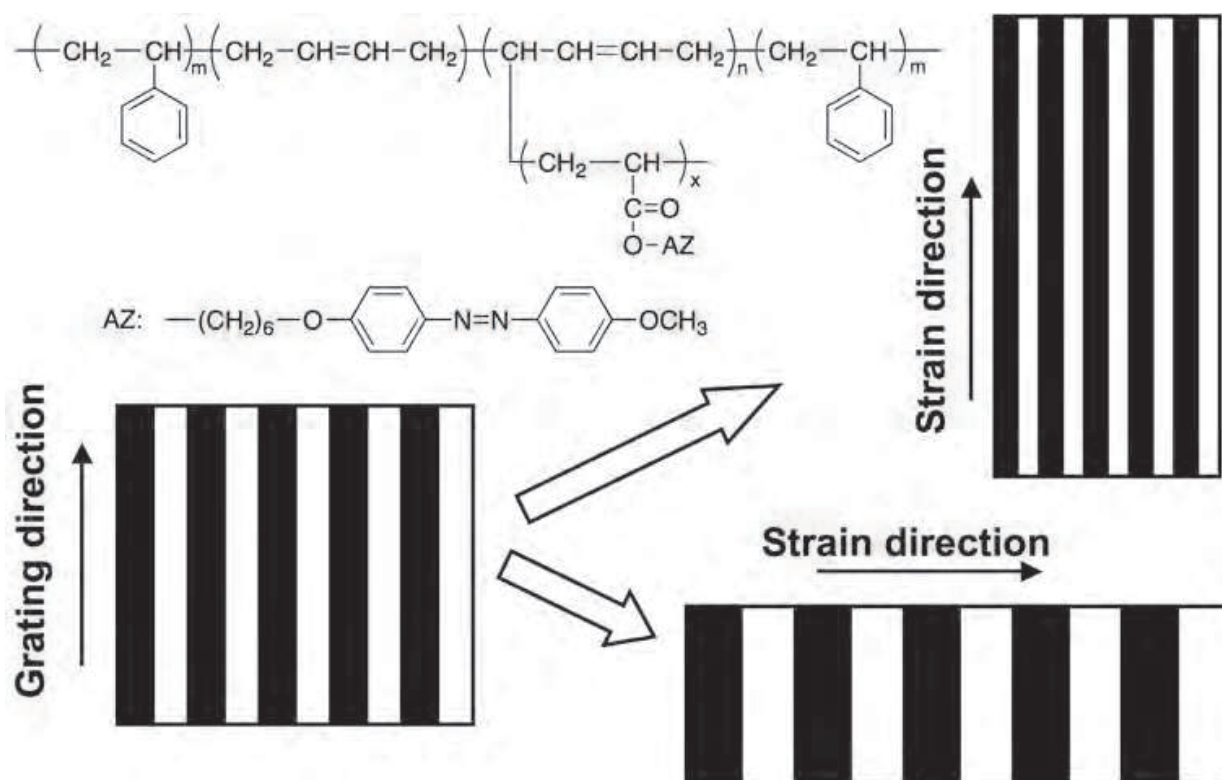


Fig. 13. Mechanically tunable fringe spacing of gratings recorded in an AZ-containing block copolymers with thermoplastics.



Generally, the fringe spacing could be decided by the pattern of the used photomask, when the grating was recorded with one writing beam. On the other hand, holographic gratings were also inscribed in block copolymer films by two coherent laser beams with an equal intensity. The recorded fringe spacing can be evaluated by  $\Lambda = \lambda w / (2 \sin \theta)$ , where  $\lambda w$  and  $\theta$  are the wavelength and the incident angle of the writing laser beams, respectively. Once the writing beams are obtained, the fringe spacing is fixed. Tunable features of the fringe spacing were achieved in films of the thermoplastic block copolymers (Figure 13). When the strain direction was parallel to the grating direction, the fringe spacing was decreased. On the contrary, the fringe spacing was increased when the strain direction was perpendicular to the grating direction. By the stretching, diffraction efficiency of the gratings was adjusted accordingly (Zhao et al., 2002). Recently, mechanically tunable fringe spacing was also obtained in gratings recorded with ABA-type triblock copolymers showing properties of conventional thermoplastic elastomers, in which rubbery poly(*n*-butyl acrylate) was designed as middle soft block and photoresponsive polymers acted as hard block (Cui et al., 2004).

## 5. Novel AZ-containing materials

Recent progress in chemistry and material science enables one to freely design functional materials with suitable processes to satisfy the need of advanced materials for a variety of applications. Integration of AZ materials with other functionalized materials and processing provides the designed materials for holograms with special features. For instance, graphene nanosheet grafted with AZ-containing polymer brushes was prepared via a “grafting-from” approach, which was used as dopant for an AZ-containing molecular glass in recording gratings (Wang et al., 2011). The diffraction efficiency of the inscribed gratings was enhanced due to the mass transfer of the graphene nanosheets showing a high refractive index. Chemically crosslinking of AZ-containing polymer films with surface-relief gratings could fix the obtained surface modulation, producing permanent shape change (Zettsu et al., 2008).

As shown in Figure 2, the Raman-Nath hologram recorded in a thin film exhibited a theoretically maximum diffraction efficiency of about 34%. This was far lower than the Bragg-type hologram in a thick film with a maximum diffraction efficiency of 100%. Furthermore, angular multiplicity could be easily obtained in the Bragg hologram, enabling thick films to be suitable for volume storage. To prepare thick and transparent films, amorphous and highly transparent PS blended with their block copolymers containing an AZ block as the minority phase to eliminate the scattering by utilizing the nanoscale microphase separation (Häckel et al., 2005, 2007). Since all of the mesogens were confined in nanospheres dispersed in PS matrix, thick and optically transparent films were obtained by injection-molded method. These films showed good angle-multiplexing capability, in which 200 holograms were superimposed and reconstructed independently at the same spot and more than 1000 write/erase cycles were successfully obtained.

However, the density of photoresponsive mesogens in the block copolymer blend systems was very low, leading to a low diffraction efficiency of the recorded gratings. To induce a large change in refractive index and record Bragg gratings with high diffraction efficiency, a series of amorphous random copolymers with both AZ moieties and photoinert mesogens was prepared, as shown in Figure 14 (Saishoji et al., 2007; Ishiguro et al., 2007). The highly transparent PMMA was utilized as substrate, when  $x > 50$  mol% in the materials preparation. Cyanobiphenyl and tolane groups were selected as the photoinert part to

enhance the refractive-index modulation. AZ mesogens with a low content to the Z = about 5 mol%, which acted as photoresponsive moieties. Transparent and thick films ( $> 100 \mu\text{m}$ ) were fabricated using a melting and pressing process.

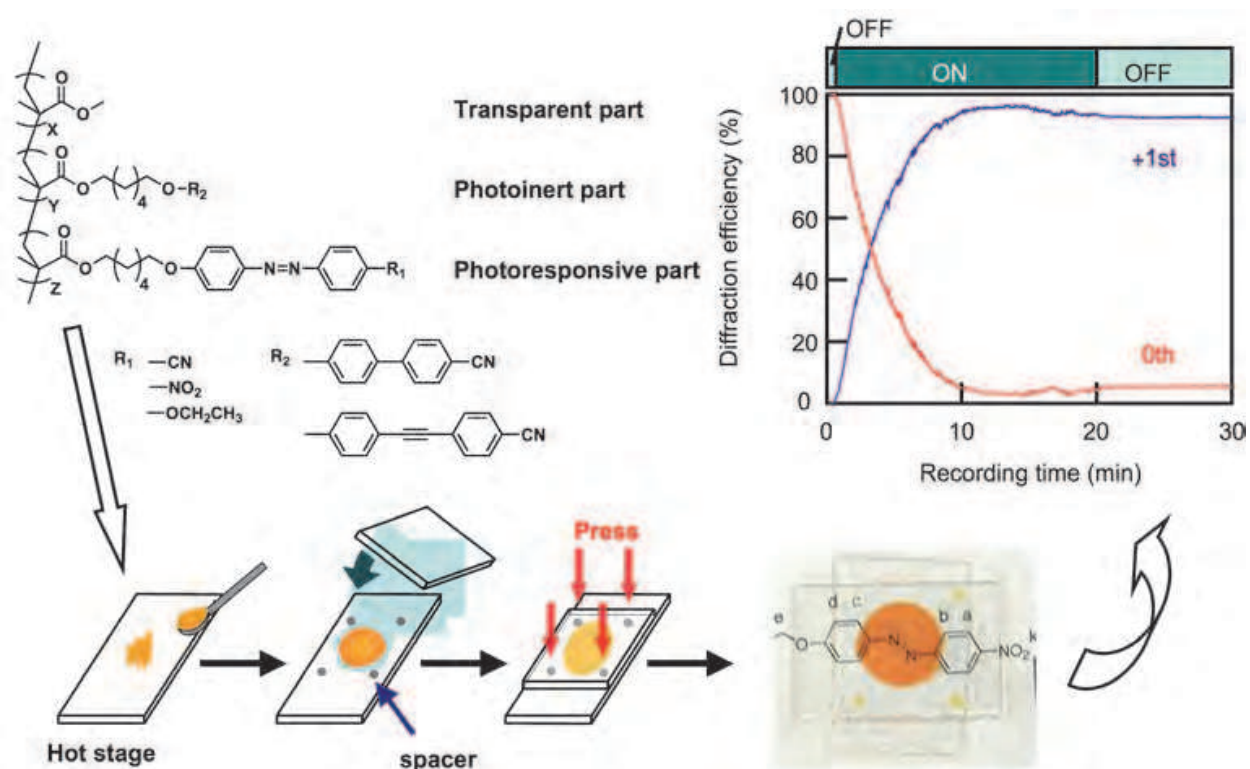


Fig. 14. Transparent and thick films of AZ-containing copolymers for Bragg gratings.

Upon irradiation with the writing beams, the first-order diffracted beam (+1st) appeared immediately and the intensity of the zeroth-order beam (0th) decreased (Figure 14). The maximum diffraction efficiency reached above 98 % in all the prepared films. Furthermore, the polarization-selective multiple holographic data storage could be obtained using the photoinduced anisotropy as well as rewritable holographic recording with about 100% diffraction efficiency. These materials prepared by a simple but balanced formulation would provide a new guideline for the construction of high-performance holographic devices.

## 6. Conclusion

Recent advance in AZ-containing materials has enabled one to record both Raman-Nath and Bragg holograms. Among these materials, low-molecular-weight compounds and amorphous polymers showed good capability of surface-relief grating formation. In LC polymers, refractive-index gratings are often recorded, accompanying with surface-relief modulation. Block copolymers with well-defined structures can eliminate the scattering of visible light by microphase separation and prohibit surface deformation when AZ blocks forms the minority phases. Furthermore, thick films ( $> 200$  microns) with good optical transparency can be prepared with random copolymers or blended block copolymers, providing substrates for recording volume holograms.

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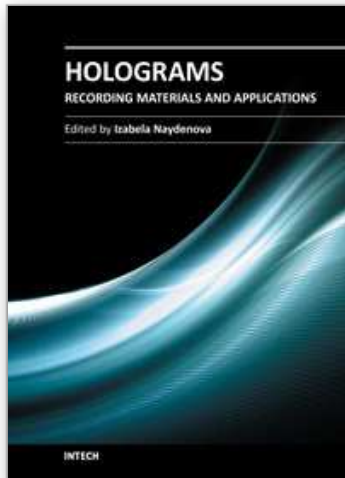
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Edited by Dr Izabela Naydenova

ISBN 978-953-307-981-3

Hard cover, 382 pages

**Publisher** InTech

**Published online** 09, November, 2011

**Published in print edition** November, 2011

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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Haifeng Yu and Takaomi Kobayashi (2011). Azobenzene-Containing Materials for Hologram, Holograms - Recording Materials and Applications, Dr Izabela Naydenova (Ed.), ISBN: 978-953-307-981-3, InTech, Available from: <http://www.intechopen.com/books/holograms-recording-materials-and-applications/azobenzene-containing-materials-for-hologram>

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