Photosensitive Materials For Holography

Roger A. Lessard

Center for Optics, Photonics and Lasers, Department of Physics, Faculty of Sciences and Engineering, Laval University, University City, Québec, Canada G1K 7P4

Gurusamy Manivannan

Surfacine Consumer Products, One Industrial Way, Tyngsboro, Massachusetts 01879

Photosensitive polymers are becoming increasingly important for holographic applications. Commercially available polymers have proved essential to the development of holography as a tool to prevent counterfeiting, for holographic optical elements, as media for display holography, as well as media for waveguiding and to make optical interconnects. Simple polymers such as PVA, PAA, PVCz and PMMA were shown to be quite useful in the field of polarization holography, real-time holography, and non-linear optics. High real-time diffraction efficiency as achieved with dye doped dichormated polyvinyl alcohol (DCPVA) and polyacrylic acid (DCPAA) opens the door to a more extensive usage of these polymers for specific applications. However, development procedures and fabrication techniques have to be established to permit broad utilization of these simple and inexpensive recording media.

Journal of Imaging Science and Technology 41: 228–232 (1997)

Introduction

Owing to the increasing importance of optical communications, a significant increase in the demand for optical devices is also arising. Consequently the demand for better materials with desirable characteristics such as high resolution, better energy sensitivity, broad wavelength response, simpler processing, and erasability has also arisen. The increased emphasis on compactness, speed of operation and wavelength selectivity has also focused a great deal of attention on solutions offered by all-optical devices and by hybrid electro-optical systems as partial replacements for electronic systems. Examples of such devices are optical components, including switches, modulators, 3D storage devices, holographic optical elements, scanners, and wavelength division multiplexers. The performance of these optical devices depends to a great extent on the performance and durability of the optical materials employed.

Polymers are excellent materials for many applications owing to their interesting properties. They may be used as substrates as well as media in standard information storage systems. Polymers doped with metal ions and/or dyes represent an important improvement for optical data storage technology for achieving high information density and rapid access memories. Organic dye doped polymers can be used for "Read-Write" memories and metal ion doped polymers are useful for "Write-Once-Read-Many" (WORM) self-developing memories.

Recording Materials

Many state-of-the-art reviews on holographic materials have documented specific aspects in detail.[1–14] Evidence of the interest in this field of research can be seen from the large number of contributions reporting various formulations and processes. This paper will point out some aspects that can be taken into account when one wants to select a recording material for a specific application.

As shown in our previous studies,[8,10] materials may be classified into three major categories, depending on the holographic recording mechanism and the nature of the materials. This system of classification is shown as a flow chart in Fig. 1, which also illustrates representative materials under each category.

Photopolymerizable Systems

Photopolymerizable systems are generally compositions consisting of a photopolymerizable monomer, a photoinitiator, and a sensitizer.[15] These systems can be used either as liquid compositions in a cavity or as dry films cast in a mold or on a substrate. In principle they can achieve quite high efficiency because a single photon can initiate a chain reaction involving a large number of reactive monomer molecules.[10,13,15]

Liquid Compositions. Close *et al*.[16] in 1969 were the first to report use of photopolymers for volume hologram recording. They used a composition comprising a dye, (methylene blue), p-toluenesufininc acid sodium salt, and metal acrylates. They were able to record holograms using a ruby laser at 694 nm with an exposure of ca. 300 mJ/cm^2 for a diffraction efficiency of 45%. Following this first attempt many authors published papers concerning this specific photopolymerizable system.[7]

At the same time, researchers in the Soviet Union were also working on similar photopolymerizable systems. Mikaelian and Barachevsky[17] presented detailed descriptions of these systems, including photopolymerizable compositions (PPCs) based mainly on a class of acrylate oligomers, such of oligourethane acrylate (OUA), oligoether acrylate (OEA), and oligocarbonate acrylate (OCA), with a biacetyl photoinitiator. They achieved good diffraction efficiency with excellent resolution (> 2500 lines/mm).

Another type of system based on a liquid composition achieves a differential crosslink density between areas of higher and lower exposure intensity. Such a system was reported by Carré *et al*[18] who developed a series of materials having response ranging from 450 to 800 nm.[12,18–20] The sponge-forming monomer was typically a multifunctional

Original manuscript received January 3, 1997.

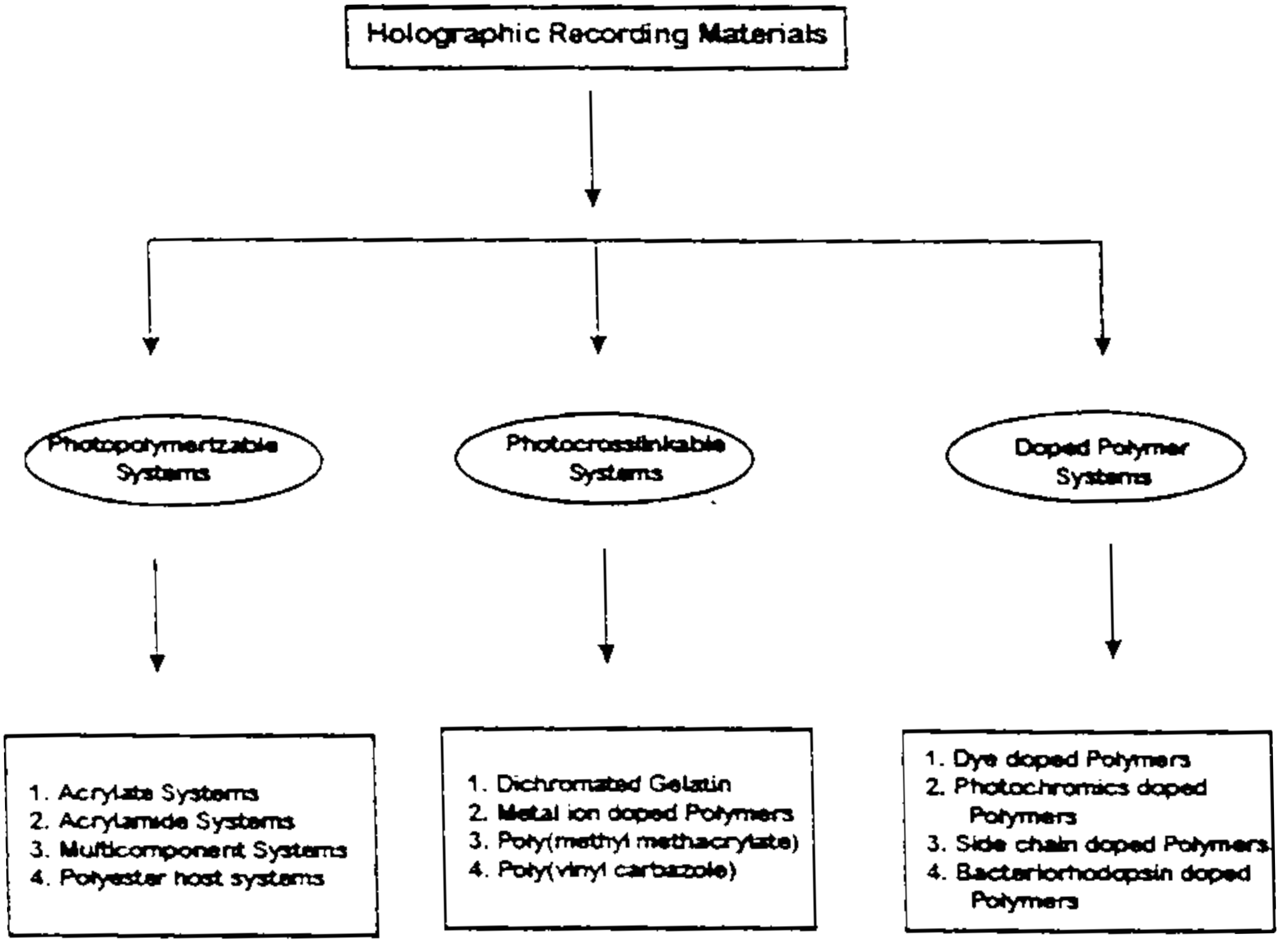


Figure 1. Flow chart describing the various catergories of holographic recording materials.

acrylate. It was associated with various low functionality acrylate monomers, a sensitizing dye, an amine co-synergist, and occasionally, specific additives or transfer agents which improved recording characteristics. Diffraction efficiencies up to 90% were achieved with almost a flat frequency response from 500 to 2500 lines/mm.

Dry Films. In this section we focus some of the most important systems only. They normally need a post-treatment, which serves to increase modulation and eliminate residual photosensitivity. Du Pont's Omnidex® is one of the most attractive photopolymers for holographic recording. This system can be sensitized to either the red or the blue-green spectral region. It can record holograms with 100% diffraction efficiency and exposure energy between 50 to 100 mJ/cm^2. Thermal processing is used to enhance the change in refractive index achieved during hologram recording. In recent years this material has largely been used for display holography, and as a security medium, to protect identification cards, drivers' licenses, etc.[7,12,22]

Polaroid's DMP-128 system is based on a mixture of acrylates, difunctional acrylamides, and a polyvinylpyrrolidone binder. Recording of a hologram requires an exposure between 5 and 30 mJ/cm^2 and the diffraction efficiency achieved ranges from 80 to 95% depending on exposure. This system is less attractive because incubation in a humid environment prior to exposure, blanket exposure to a (uniform) white light source in addition to the imaging exposure, and treatment in a liquid developer composition, followed by a rinse to remove processing chemicals and careful drying, are all required after exposure.[7,12,23,24] It has, however, proved useful for specific applications.

Other systems have also been studied and reviewed.[7,10–12] Tomlinson *et al.*[25] have described systems based on the MMA monomer; Bloom *et al.*[26] have described polyester host systems. Tomlinson *et al.*[27] proposed use of multicomponent monomer systems, and acrylamide based systems have been reported by Sugawara *et al.*[28] and by Jeudy and Robillard.[29]

Photocrosslinkable Systems

Photocrosslinkable systems constitute a major class of recording materials. Different sensitizers such as metal ions and dyes can be employed to sensitize the polymer matrix. On exposure to an appropriate light source, the sensitizer undergoes photochemical changes leading to refractive index modulation and hologram formation. Most of these materials are used in the form of dry films. They can be classified as biopolymers and synthetic polymers.

Biopolymers. Dichromated gelatin has been the most widely used polymer for applications such as the fabrication of holographic optical elements, heads-up displays, laser scanners, fiber optic couplers, and optical interconnects. Some organic dyes can also be used to render the film sensitive to a specifically selected wavelength. A good review of this system can be found in many books.[1,2,25] This particular recording system is unique, and the photochemical

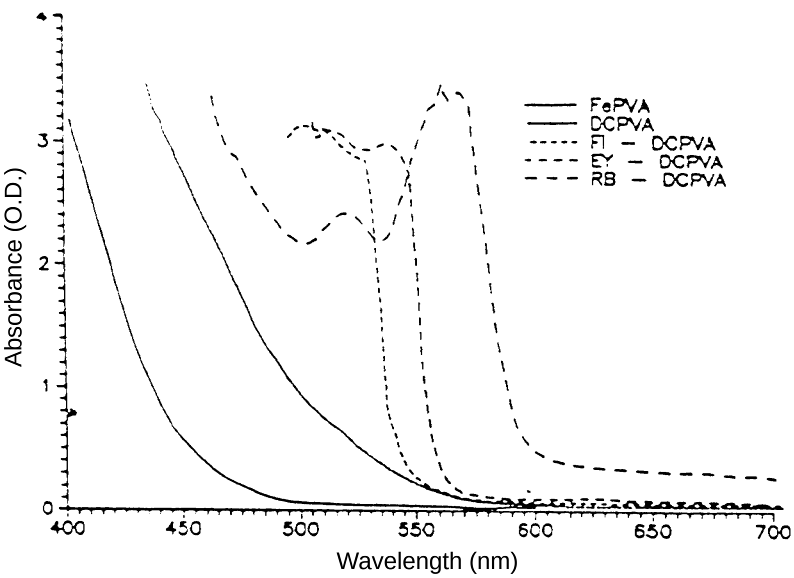


Figure 2. The absorption spectra of the FePVA, DCPVA and Dye-sensitized DCPVA systems: Fl-DCPVA, Fluorescein-DCPVA; EY-DCPVA, Eosin Y-DCPVA, and Rose-Bengal-DCPVA.

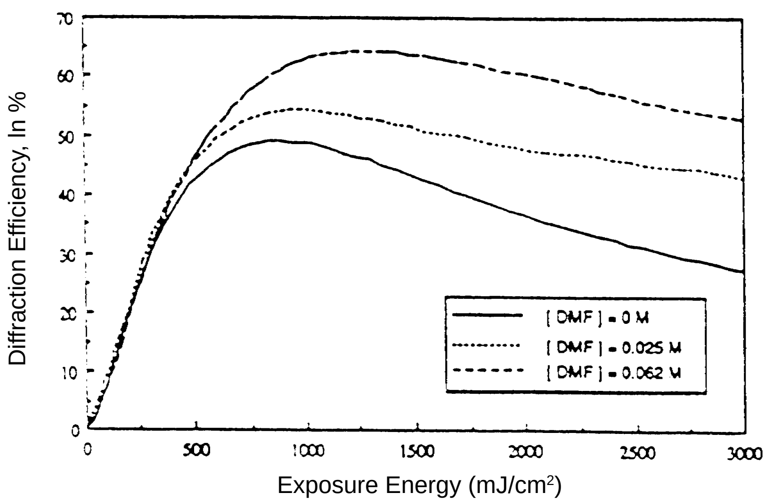


Figure 3. Real-time diffraction efficiency profiles of DCPVA with and without DMF as a function of the exposure energy.

process can be accelerated by addition of an appropriate dye, which also alters the recording wavelength.[26-29]

Synthetic Polymers. Metal ions such as Cr(VI) and Fe(III) have been doped into various polymer matrices such as polyvinyl alcohol (PVA) and polyacrylic acid (PAA) to enable holographic recording.

Fabrication of metal ion doped polymer films has been described before.[11] The absorption spectra of Ferric chloride doped PVA (FePVA) and dichromated poly(vinyl alcohol) (DCPVA) doped with various dyes such as fluorescein, eosin Y, and rose bengal are shown in Fig. 2 to demonstrate that these media can be made sensitive to particular wavelengths.

As in the case of dye-doped dichromated gelatin, it was found that addition of electron donors as well as other dopants significantly influences diffraction efficiency of the holograms recorded in these media. In a survey of different dopants, it was found that dimethylformamide (DMF) was the most effective. Figure 3 depicts the influence of this additive, by comparison of the real-time diffraction efficiency profiles of DCPVA with and without DMF. One can see that at optimum conditions, a diffraction efficiency of 45% without DMF can be increased to ca. 65% when it is added. However it was also found that using PVA doped with xanthene dyes permitted further increase in diffraction efficiency. Figure 4 shows that real-time diffraction efficiency of DCPVA doped with fluorescein reaches ca. 60%. The xanthene dyes serve not only as wavelength extenders, but also as electron donors, which increase the crosslinking efficiency of the materials, thus contributing to enhancement of the diffraction efficiency.

This efficiency can be further improved if we employ a very simple developing process. In effect, by immersing the hologram after exposure in absolute ethanol at 70°C for 10 min and drying with an air blower, we were able to achieve a diffraction efficiency of up to 72% (see Fig. 7 in Ref. 11). Development in this manner does represent a constraint, but confers the additional advantage of rendering the film insensitive to light.

Ferric chloride doped PVA (FePVA) is another very simple system that can be used in many applications. As for DCPVA, FePVA can be doped with dyes to define the writing wavelength. FePVA can also be used in real time as well as after development. Consequently PVA systems represent a very simple and inexpensive approach for those who want to make their own holographic media. The systems can be used as either thin or thick films, and can be

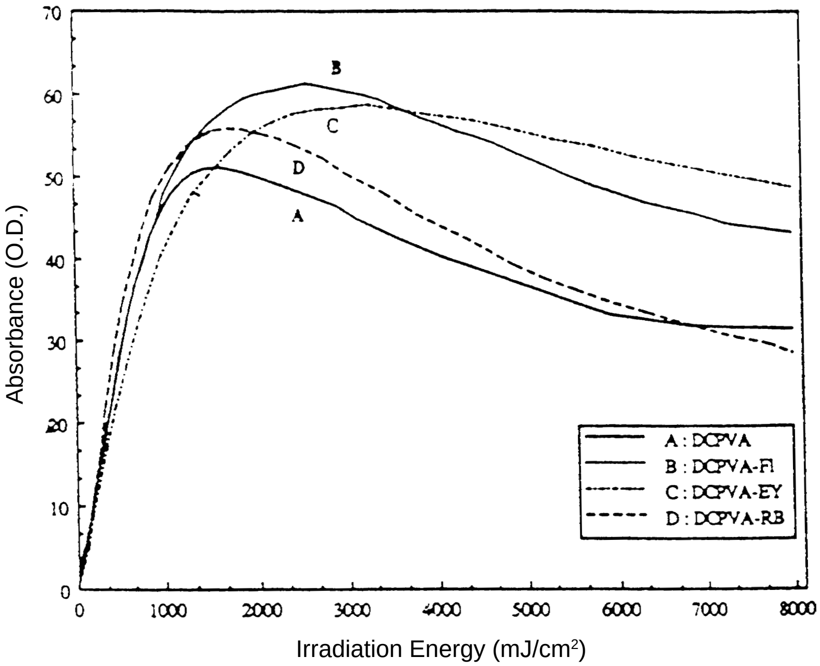


Figure 4. Real-time diffraction efficiency profiles for Xanthene dyes doped with DCPVA: PVA = 7 wt%; $(NH_4)_2Cr_2O_7$ = 1,2 wt%; fluorescein = 5×10^{-4} M; eosin Y = 5×10^{-6} M; and rose bengal = $2,4 \times 10^{-4}$ M.

spin coated. With a good diffraction obtained therewith and their high resolution makes the films very attractive.

Another synthetic polymer that is very attractive is polyacrylic acid (PAA) doped with metal ions. Different dichromated PAA (DCPAA) films have been prepared from coating solutons incorporating varying weight percentages of PAA ranging from 5 to 25%, keeping constant amount of ammonium dichromate (2.0 wt.%). We found that films formulated with the higher concentration of PAA showed the maximum diffraction efficiency of 28%, for the case of 25 wt.% PAA, but the exposure requirement was also fairly high (4 J/cm^2). Incorporating DMF at a concentration of 2.2 M into a coating solution comprising 20 wt.% PAA and 2.0 wt.% ammonoium dichromate led to films with a diffraction efficiency of more than 50% at an energy density of about 250 mJ/cm^2 (Fig. 9 of Ref. 11). This result suggests that this recording system is also potentially useful with ease in many applications.

Doped Polymer Systems

Dye-doped polymer systems are important recording materials, since they are able to record polarization holograms. Many authors[30,32] followed the pioneering work of Kakischasvili[32] and studied different dye-doped PVA systems as media for recording polarization holograms. Many basic research papers concerning these particular doped polymer systems can be found in our Milestone Series.[10]

Photochromic Systems

The photoreversible color change between thermally stable and metastable states of photochromic molecules can be used to modulate the absorption and refractive index of a polymer film doped with these molecules. Investigations at Laval University[34–36] concerned two kinds of polymer, polyvinyl carbazole (PVCz) and polymethyl methacrylate (PMMA), along with two different photochromic spiropyran dyes (PVCz:SP and PMMA:SP, respectively). The films were cast from a chloroform solution of the polymer and the dye. All films were prepared by gravity settling under normal laboratory conditions (20°C, 10% relative humidity for PVCz and 35 to 45% relative humidity for PMMA during 72 h). Films of different thickness ranging from 10 to 250 μm as measured with a Sloan Dektak IIa profilimeter were obtained by variation of the volume of the coating solution.

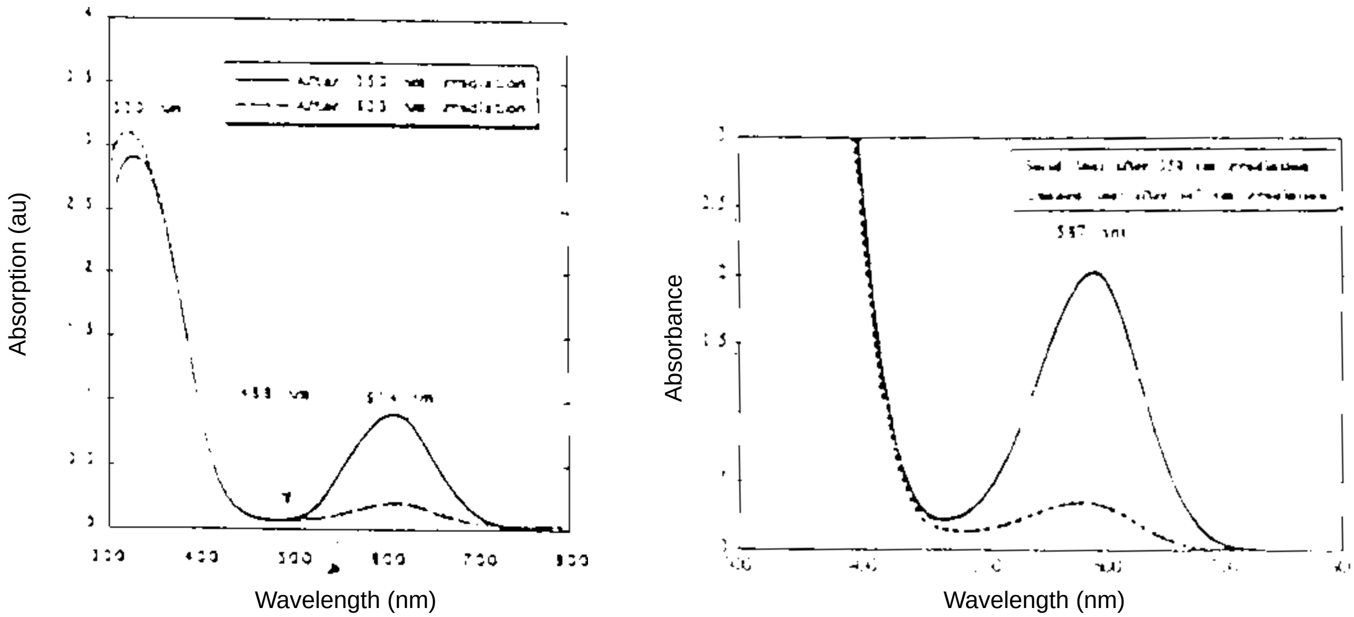
An experimental setup involving three different lasers enabled write-read-erase (WRE) cycling of the media. A Kr laser emitting at 350 nm was used to write; the reading beam was derived from an Ar laser at 488 nm; and the erasing beam came from a He-Ne laser emitting at 633 nm. The absorption spectra of the spiropyran in PVCz and PMMA are shown in Figs. 5(a) and 5(b). We found that the real-time diffraction efficiency of a holographic grating recorded with an exposure energy of 300 mJ/cm^2 was 10.5% for a PVCz:SP film thickness of 12 μm, but was much less (ca. 0.5%) for PMMA:SP films of the same thickness.

Our experiments[33,34] also showed that more than 100 WRE cycles could be carried out without any apparent fatigue of the material. In these experiments energy of the writing pulse was 10 mW/cm^2 with a duration of 800 ms; the energy of the erase pulse was 20 mW/cm^2 for 4 s. However, it is known that spiropyrans do suffer from degradation after many repetitive recording cycles.

Conclusions

Dye doped polymers are becoming increasingly important for holographic applications. Commercially available polymers have proved essential to the development of holography, as a tool to prevent counterfeiting, for holographic optical elements, as media for display holography, and as media for waveguiding and making optical interconnects.

Simple polymers such as PVA, PAA, PVCz, and PMMA were shown to be quite useful in the field of polarization holography, real-time holography, and nonlinear optics. High real-time diffraction efficiency as achieved with dye doped dichormated polyvinyl alcohol DCPVA and polyacrylic acid DCPAA opens the door to a more extensive use of these polymers for specific applications.



(a) **(b)**

Figure 5. UV-visible absorption spectra (a) PVCZ:SP; (b) PMMA:SP

References

1. L. Solymar and D. J. Cooke, *Volume Holography and Volume Grating*, Academic Press, New York, 1981.
2. G. Kaempf, H. Loewer, and M. W. Whitman, *Polym. Eng. Sci.* **27:** 1421 (1987).
3. *Polymers in Information Storage Technology*, K. L. Mittal, Ed., Plenum Press, New York, 1989.
4. R. A. Lessard, R. Changkakoti, and G. Manivannan, “Polyvinyl Alcohol Based Recording Materials for Holography and Non-linear Optics,” *Opt. Mem. Neural Net.* **1**, 75–101 (1992).
5. G. Manivannan, R. Changkakoti, and R. A. Lessard, “Cr(VI) and Fe(III) Doped Polymer Systems as Real-time Holographic Recording Materials,” *Opt. Eng.* **32**, 671–676 (1993).
6. G. Manivannan, R. Changkakoit, and R. A. Lessard, “Metal Ion Doped Polymers as Media for Opticals Memories,” *Polym. Advanc. Techn.* **4**, 569–576 (1993).
7. R. A. Lessard, R. Changkakoti, and G. Manivannan, “Holographic Recording Materials,” *Processes in Photoreactive Polymers*, V. V. Krongauz and A. S. Trifunac, Eds., pp. 307–367, Chapman and Hall (1995).
8. R. A. Lessard and G. Manivannan, “Holographic Recording Materials: An Overview,” *Proc. SPIE* **2405**, 2–22 (1995).
9. G. Manivannan, V. P. Pham, and R. A. Lessard, “Organic Materials for Optical Processing,” *Optoelectronics: Current Trends,* A. Selvarajan and K. Shenai, Eds., pp. 61–71, Tata McGraw Hill, New Delhi, India (1996).
10. “Photopolymers: Physics, Chemistry and Applications,” R. A. Lessard and G. Manivannan, Eds. *SPIE Milestone Series* **MS114**, SPIE Optical Engineering Press, Bellingham, Washington, 1995.
11. G. Manivannan and R. A. Lessard, “Metal-ion doped polymers: Holographic Characterization, Mechanisms and Applications,” *Polymers in Optics: Physics, Chemistry and Applications*, R. A. Lessard and W. F. X. Frank, Eds., **CR 63,** 307–333 (1996).
12. D. J. Lougnot, “Self-processing photopolymer materials for holographic recording,” *Polymers in Optics: Physics, Chemistry and Applications*, R. A. Lessard and W. F. X. Frank, Eds., 1996, pp 190–213.
13. S. A. Ekhorutomwen and S. P. Sawan, “A Critical Review on Photoresists,” *Polymers in Optics: Physics, Chemistry and Applications*, R. A. Lessard and W. F. X. Frank, Eds., 1996, pp 214–238.
14. A. S. Dvornikov and P. M. Rentzepis, “Reaction kinetics of photochromic materials and their application to 3D optical memories,” *Polymers in Optics: Physics, Chemistry and Applications,* R. A. Lessard and W. F. X. Frank, Eds., 1996, pp 239–261.
15. A. Reiser, *Photoactive Polymers*, Wiley, New York, 1989; J. P. Fouassier and J. F. Rabek, *Radiation Curing in Polymer Science and Technology*, vols. I and II., Elsevier, London, 1993.
16. D. H. Close, A. D. Jacobson J. D. Margerum, R. G. Brault, and J. J. McClung, *Appl. Phys. Lett.* **14**, 159.
17. A. L. Mikaelian and V. A. Barachevsky, *Proc. SPIE* **1559**, 246 (1991).
18. C. Carré, D. Ritzenthaler, D. J. Lougnot, and J. P. Fouassier, *Opt. Lett.* **12**, 646 (1987).
19. D. J. Lougnot, D. Ritzenthale, C. Carré, and J. P. Fouassier, *J. Appl. Phys.* **63**, 4841 (1988).
20. C. Carré and D. J. Lougnot, “Developments of Recording Materials Based on the Photopolymerization of Monomers and Oligomers,” *OPTO ’90*, ESI Publications, Paris, 1990, p. 165.
21. N. Noiret-Roumier, D. J. Lougnot, and I. Petitbon, “Photopolymer Materials for Holographic Recording in the Red and Near Infra-Red,” *OPTO ’92*, ESI Publications, Paris, 1992, p. 104.
22. B. M. Monroe, W. K. Smothers, D. E. Keys, R. R. Krebs, D. J. Mickish, A. F. Harrington, S. R. Schicker, M. K. Armstrong, D. M. T. Chan, and C. I. Weathers, *J. Imaging Sci.* **35**, 25 (1991).
23. R. T. Ingwall and H. L. Fielding, *Opt. Eng.* **24**: 586 (1989).
24. D. H. Whitney and R. T. Ingwall, *Proc. SPIE* **1213**, 18 (1990).
25. H. I. Bjelkhagen, “Selected Papers on Holographic Recording Materials,” *SPIE Milestone Series* **MS130**, SPIE Optical Engineering Press, Bellingham, Washington, 1995.
26. A. Graube, *Opt. Commun.* **8**, 251 (1973).
27. C. Solano, R. A. Lessard, and P. C. Roberge, *Appl. Opt.* **26**, 1989 (1987).
28. N. Capolla and R. A. Lessard, *Appl. Opt.* **27**, 324 (1988).
29. J. Blyth, *Appl. Opt.* **30**, 1598 (1991).
30. L. Nikolova and T. Todorov, *Opt. Acta* **24**, 1179 (1977).
31. S. Calixto and R. A. Lessard, *Appl. Opt.* **23**, 1989 (1984).
32. J. J. A. Couture and R. A. Lessard, *Appl. Opt.* **27**, 3368 (1988).
33. Sh. D. Kakischasvili, *Opti. Spektrosk.* **33**, 324 (1972).
34. R. A. Lessard, F. Ghailane, and G. Manivannan, “Photochromism and its applications in real-time holography” *Photoactive Organic Materials*, F. Kajzar et. al., Eds., Kluwer Academic Publishers, Norwell, MA, 1996, 325–341.
35. F. Ghailane, Ph.D. Thesis, “Étude du photochromisme et de la photoréfractivité dans le poly(vinylcarbazole),” Université Laval (1995).
36. S. S. Xue, G. Manivannan, and R. A. Lessard, *Thin Solid Films*, **253**: 228 (1994).