# PROCEEDINGS OF SPIE

# Quantitative roadmap of holographic media performance

Benjamin A. Kowalski, Robert R. McLeod

**SPIE.**

# Quantitative roadmap of holographic media performance

Benjamin A. Kowalski*, Robert R. McLeod
Dept. of Electrical, Computer, and Energy Eng., Univ. of Colorado at Boulder
425 UCB, Boulder, CO USA 80309

## ABSTRACT

For holographic photopolymer media, the "formula limit" concept enables facile calculation of the fraction of writing chemistry that is usefully patterned, and the fraction that is wasted. This provides a quantitative context to compare the performance of a diverse range of media formulations from the literature, using only information already reported in the original works. Finally, this analysis is extended to estimate the scope of achievable future performance improvements.

**Keywords:** photopolymers; holography; optical data storage; reaction/diffusion kinetics; diffractive optical elements

## INTRODUCTION

In holographic photopolymers, optically driven diffusion generates refractive index modulations, via compositional modulations of an initially homogeneous mixture of two index-contrasting components. This diffusive mechanism is "self-processing" i.e. does not require a wet chemical processing step, in contrast to other photopolymer patterning techniques (e.g. solvent wash for photoresist or micro-stereolithography). This makes it an appealing material platform for applications which require thick media layers that are not suitable for wet processing.

These include applications in which the recorded index modulations serve either as images (e.g. data storage, display holography) or as optical elements (e.g. custom GRIN components, integrated optical devices). All of these applications are characterized by simultaneous stringent requirements on both optical properties (achievable index modulation, sensitivity) and mechanical and process properties (cheap, stable, mechanically rugged).

This set of simultaneous requirements means that materials design involves a series of delicately balanced tradeoffs [1]. For example, increasing the volume fraction of the writing chemistry (as opposed to the inert binder or host matrix) will increase the index modulation of recorded features (the "signal" term) but will also increase recording-induced optical scatter (often the dominant "noise" term). Furthermore, it will also increase the recording-induced volume shrinkage, which leads to distortion of recorded features, especially in thick samples.

Thus, good "signal-to-noise" recording performance is achieved through, first, maximizing the index-contrast benefit achieved per bond converted, and second, minimizing the shrinkage and scatter penalties accrued per bond converted. The index-contrast benefit is typically pursued via synthesis of monomers containing a large number of index-contrasting groups per reactive group, within the constraints imposed by solubility in the organic matrix and diffusivity [2]. The scatter penalty per bond converted can be minimized by adjusting the recording kinetics to suppress the self-amplification of so-called parasitic or noise gratings, which are typically the dominant source of recording-induced scatter [3]. Finally, the shrinkage penalty per bond converted can be minimized by using ring-opening writing polymerizations, in which this shrinkage is partially compensated by a volume increase due to ring-opening [4] [5].

This brief discussion hints at the proliferation of diverse design strategies pursued in holographic photopolymer media over the last two decades, further illustrated schematically in Figure 1. We will show below that the "formula limit" concept enables quantitatively meaningful comparisons among these various media formulations, in terms of the achievable recording fidelity. It should be emphasized that this formula limit can be calculated using only readily available data about the media components, and does not require the development of a comprehensive quantitative reaction/diffusion model. To show the ease and utility of this calculation, we perform it for a range of significant formulations from the literature. This calculation also enables an estimate of how much further improvement in index modulation is possible for this class of media.
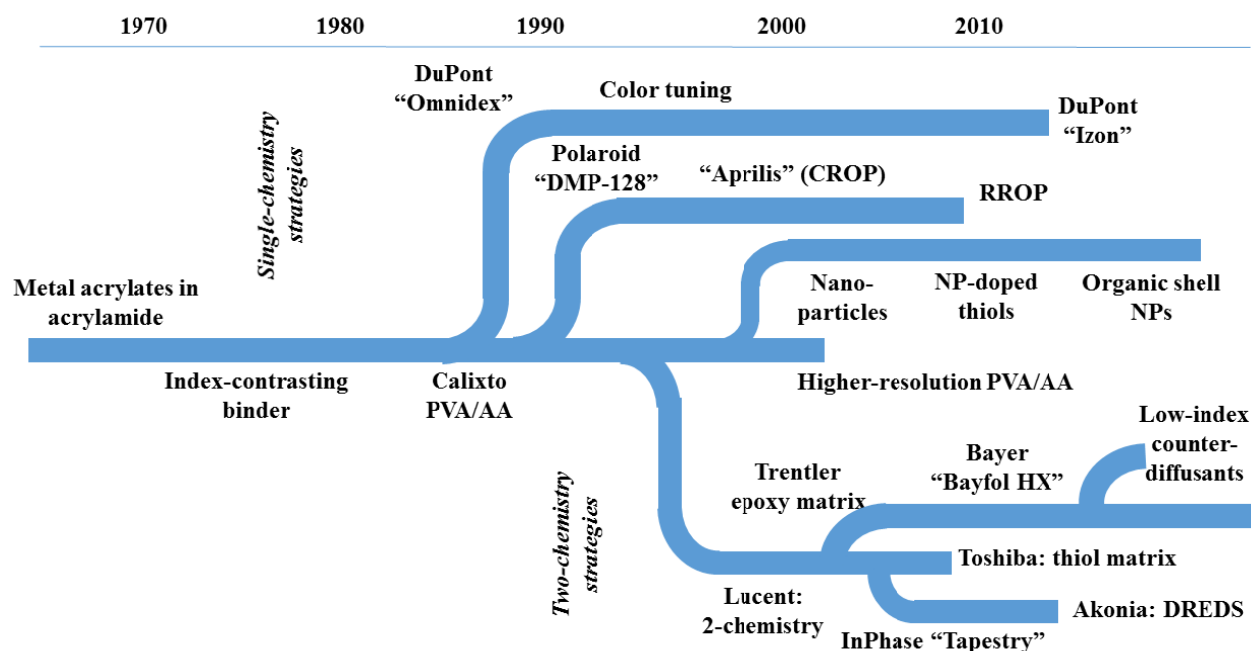
Figure 1. An evolutionary tree of holographic photopolymer formulations of particular academic or commercial significance. Design strategies fall into two general categories: single-chemistry, in which the same photochemistry both patterns the media and hardens it into a crosslinked network, and two-chemistry, in which a crosslinked host matrix is first formed via thermoset, a process that is orthogonal to the subsequent photo-patterning chemistry. A more quantitative survey of these same formulations follows below.

## RECORDING KINETICS

First we consider the general mechanisms by which the reaction/diffusion kinetics of recording can impose limits on the recording fidelity and spatial resolution, causing some fraction of the polymerized writing monomer to be wasted, i.e. to be spatially distributed with something other than the desired patterning. This wasted fraction is often surprisingly large, as will be seen below, and therefore must be taken into account in any program for rational design of media. The general mechanisms for waste can be categorized by the affected spatial frequencies of recording.

First, recording at low spatial frequencies can be suppressed by interrupted diffusion of writing monomer. This interruption can be due to the well-known Zhao and Mouroulis coupling of reaction and diffusion, which gives rise to characteristic "rabbit ears" features comprising higher harmonics rather than the intended fundamental spatial frequencies [6]. Or the interruption can be due to polymerization-induced vitrification, which can prevent full in-diffusion of monomer into large features [7].

Next, recording at high spatial frequencies can also be suppressed, due to diffusional blurring. Here, some photo-generated species undergoes significant diffusion from bright regions into dark regions before becoming immobilized. The amount of blurring is expected to scale as $1/\Lambda^2$, where $\Lambda$ is the spatial period, since this is the scaling for the time to diffuse across a fringe [8]. As seen in Figure 2, this scaling is quite general, and obtains even across media formulations with quite different underlying physical mechanisms for diffusion. For example, in [9] blurring is attributed to diffusion of short mobile chains, but in [10] it is attributed to reaction-diffusion of the radical tips of fixed chains. It should be emphasized that this scaling enables the prediction of the media resolution limit (i.e. the high spatial frequency at which the patterned index response falls to zero) from experimentally accessible measurements at lower spatial frequencies.

Thus, due to some combination of the above mechanisms, the recording process in any particular media will be governed by a characteristic transfer function in the spatial frequency domain. This transfer function may be associated with

undesirable effects, including strongly reduced diffraction efficiency of high-spatial-frequency reflection holograms (as in e.g. display or spectral filter applications). But if the transfer function is well matched to the desired recording spatial frequencies, it may instead lead to beneficial suppression of high-spatial-frequency scatter noise or low-spatial-frequency aberrations in the recording beam. In the survey of media formulations below, we will not attempt to account for these effects, but will only consider the usable $\Delta n$ only at the spatial frequency of the reported experiments.
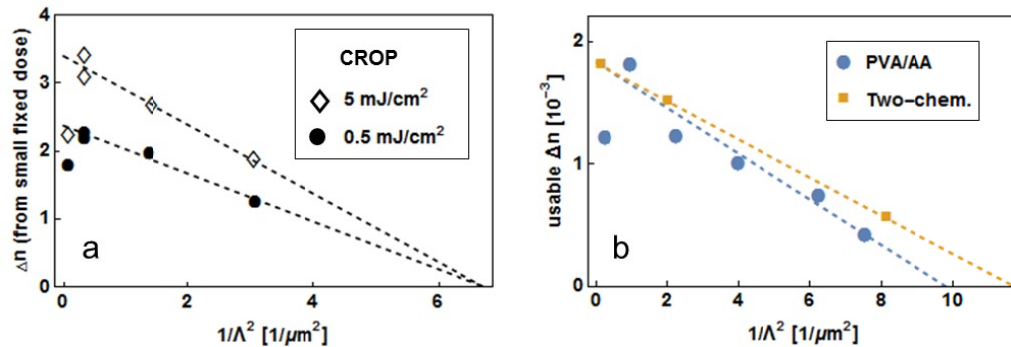


Figure 2. Index response $\Delta$n plotted against inverse square of grating pitch $\Lambda$, showing that different classes of media exhibit the same characteristic scaling of diffusional blurring. Dashed lines are fits to reported data; their x-intercepts indicate the media spatial resolution limit. (a) CROP media [11]; note that the same resolution limit obtains at two different exposure intensities. (b) Acrylamide media [10] and two-chemistry media [9].

Finally, even after the above mechanisms have all been accounted for, some additional wasted fraction may exist regardless of spatial frequency. For example, in some two-chemistry media, chain transfer effects give rise to short unattached chains of writing polymer, which then diffuse away to produce an unwanted uniform background index change [9]. Any such uniform background component to the recorded index feature will be invisible to Bragg detection.

A full understanding of all of these effects in a particular media formulation requires a comprehensive quantitative model of the various reaction/diffusion processes. Obtaining such a model typically requires a substantial investment of research effort, because of the special difficulties in characterizing the kinetics of coupled processes with sub-micron spatial scales and sub-millimolar concentrations. However, in the following section we will demonstrate that, even in the absence of such a comprehensive kinetic model, it is still possible to obtain salient insights into the recording fidelity simply by comparing the usable $\Delta n$ to the readily calculated "formula limit."

## FORMULA LIMIT CONCEPT

We define the "formula limit" as the theoretically achievable index modulation, in the limit of ideal spatial patterning of all components. This can be straightforwardly derived from only the volume fractions and index contrast of the components, using the Lorentz-Lorenz relation for mixtures [12]. In the limit of a small volume fraction of weakly index-contrasting writing polymer undergoing ideal volume displacement, it is well approximated as [10]:

$$\Delta n_{formula} = (n_{writing\ polymer} - n_{matrix})\varphi_{writing\ polymer}$$

In practice, the achievable index modulation $\Delta n$ is only some (typically rather small) fraction of this limit; we call this the "usable fraction." The remaining wasted fraction must correspond to writing polymer that is not distributed with the desired spatial patterning, due to the waste mechanisms discussed above. This wasted fraction is important from a materials design perspective, not only because it fails to contribute to usable $\Delta n$, but also because it does still actively contribute to all the penalties of unwanted volume shrinkage and scatter.

To illustrate the ease and utility of this calculation, we perform it for a representative set of formulations of academic and commercial interest, whose component indices and volume fractions are already reported. First we consider, in Figure 3(a), a plot from a foundational paper in the development of two-chemistry media (i.e. thermoset host matrix and guest photopolymer) [1]. Here, usable $\Delta n$ is plotted against the quantity we have identified as the formula limit (although its physical meaning is not explicitly discussed in the text). Each data point in Figure 3(a) represents a media formulation with slightly different components, but the same underlying chemistry. The fact that the points fall roughly

on a straight line means that the usable fraction is roughly equal in all of these formulations. This roughly linear behavior, which will be exhibited again below, indicates that the recording kinetics are not strongly affected by the substitution of new components with different index but the same reactive groups. This supports the concept of the usable fraction of the formula limit as a design metric that is primarily dependent on chemical composition but largely independent of specific concentrations.
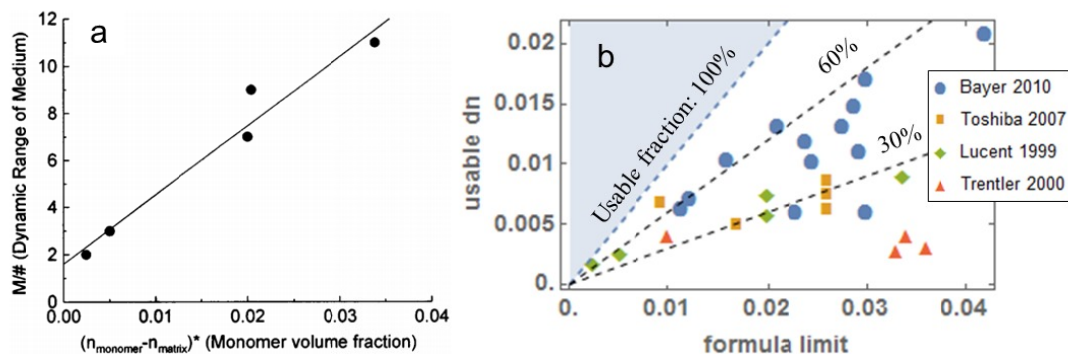


Figure 3. (a) Usable Δn of various formulations (expressed as M/#), plotted against a quantity that is equal to the "formula limit" as defined here. Reproduced from [1]. (b) The data points from (a), along with data from other similar two-chemistry formulations, from the early Trentler et al paper [13] to the more recent Toshiba [14] and Bayer [15] patents. The improvements in usable Δn within the last decade are evidently due to increases in usable fraction, rather than formula limit.

Next, Fig. 3b compares this result to later generations of two-chemistry media, revealing that the dramatic gains in dynamic range over the last decade, up to Δn ~ 0.02 to 0.04, are primarily due to improvements in the usable fraction, rather than the formula limit. These improvements have been qualitatively explained in terms of changes in the recording kinetics. For example, the matrix crosslink density can be tuned to optimize the relative rates of reaction and diffusion [15]. Alternatively, the rate of immobilization of growing polymer chains can be improved by incorporating additional reactive sites into to the matrix [9]. Even greater control of immobilization can in principle be achieved using, for example, thiol-click writing chemistry; an early proof of concept [16] is included in Fig. 4 below. The formula limit analysis presented here provides a quantitatively meaningful context for comparison of these various modifications.
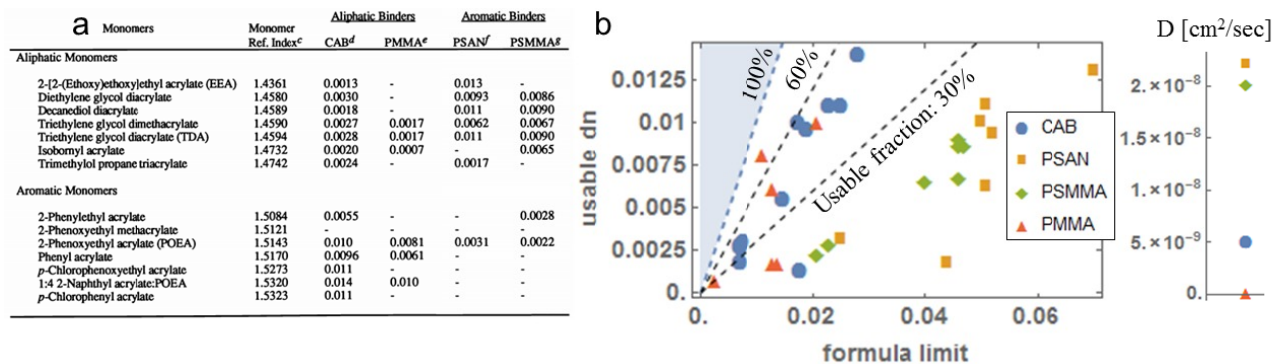


Figure 4. (a) Performance of various candidate formulations, using the same basic chemistry as later DuPont commercial media. Reproduced from [17]. (b) The same data, plotted against formula limit, showing that all formulations with a given binder tend to have a similar usable fraction in spite of their widely differering absolute Δn. Inset: reported diffusivities D for each binder. Good usable fraction is associated with low D, in contrast to some other systems.

This formula limit analysis can also be extended to other photopolymer formulations with very different chemistries. For example, ref. [17], shown in Figure 4(a), explores the basic chemistry that would go on to form the basis for DuPont holographic media, and which uses a high-molecular-weight but non-crosslinked binder. Various pairings of candidate writing monomers and binders are evaluated, leading to the expected conclusion that high-index binders should be paired with low-index monomers, and vice versa. However, an additional trend becomes apparent when the results are plotted

in terms of usable fraction (Fig. 4b): all formulations incorporating a given binder tend to have roughly the same usable fraction, even as their absolute $\Delta n$ varies widely. Furthermore, the binders with the highest usable fractions are those with the lowest reported small-molecule diffusivities (Fig. 4b inset), whereas high diffusivities are believed to be essential in many other photopolymer systems.

Next, a similar analysis can be performed for many of the other material design strategies described above, including ring-opening writing chemistries; these results are summarized in Fig. 5. In particular, it is apparent that the ring-opening formulations reported in the literature, either cationic or radical, have relatively low usable fractions. (Evidence that diffusional blurring is a significant source of waste is reported elsewhere [11].) Thus, if these fractions can be improved (as was achieved for conventional radical writing chemistries via engineering new immobilization pathways, above), this will enable a dramatic enhancement of $\Delta n$ without any sacrifice of shrinkage performance.



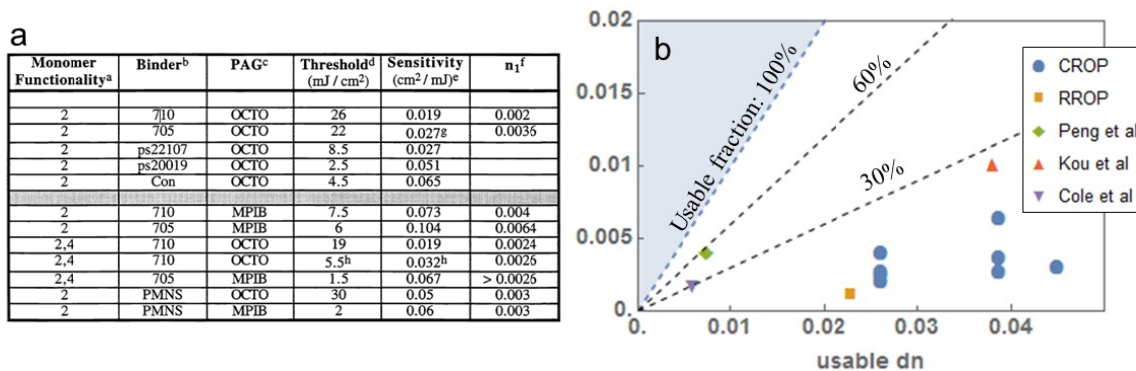| Monomer Functionality[a] | Binder[b] | PAG[c] | Threshold[d] (mJ / cm²) | Sensitivity (cm² / mJ)[e] | n₁[f] |
|---|---|---|---|---|---|
| 2 | 710 | OCTO | 26 | 0.019 | 0.002 |
| 2 | 705 | OCTO | 22 | 0.027[g] | 0.0036 |
| 2 | ps22107 | OCTO | 8.5 | 0.027 | |
| 2 | ps20019 | OCTO | 2.5 | 0.051 | |
| 2 | Con | OCTO | 4.5 | 0.065 | |
| 2 | 710 | MPIB | 7.5 | 0.073 | 0.004 |
| 2 | 705 | MPIB | 6 | 0.104 | 0.0064 |
| 2,4 | 710 | OCTO | 19 | 0.019 | 0.0024 |
| 2,4 | 710 | OCTO | 5.5[h] | 0.032[h] | 0.0026 |
| 2,4 | 705 | MPIB | 1.5 | 0.067 | > 0.0026 |
| 2 | PMNS | OCTO | 30 | 0.05 | 0.003 |
| 2 | PMNS | MPIB | 2 | 0.06 | 0.003 |

Figure 5. (a) Measured performance of various early CROP formulations. Reproduced from [4]. (b) The same data as (a), plotted in terms of usable $\Delta n$ vs estimated formula limit, along with reported data for a variety of other design strategies: Choi et al (RROP) [5], Peng et al (thiol-click) [16], Cole et al (thermoplastic matrix) [18], Kou et al (dendritic binder) [19].

## CONCLUSION

It has been shown that the formula limit and usable fraction are readily calculated for a broad range of media in the existing literature, without requiring a comprehensive quantitative kinetic model. There are, of course, limits to the applicability of this calculation. Most importantly, it requires knowledge of the mixing rule (i.e. whether the inert component undergoes perfect volume displacement leading to a purely compositional modulation, or whether some density modulation also obtains). The analysis above assumes nearly perfect 1:1 volume displacement, consistent with all of the relatively few mixing studies in two-chemistry media. If any of these media in fact exhibit a significant density modulation, then the usable fraction calculated here will be in error. In the usual case of high-index writing monomer, this density modulation will add up in phase with the expected compositional modulation, and so the present analysis will *over*-estimate the usable fraction.

This limitation notwithstanding, the formula limit analysis affords useful information to optimize the usable fraction in a broad range of media formulations. Some design strategies to improve usable fraction have already been demonstrated. Most notably, Akonia's DRED™ technology uses matrix-tethered protected radical groups to quickly immobilize writing polymer, leading to a six-fold enhancement of $\Delta n$ to 0.05 [20]. Many other strategies for matrix-tethered functionalities also appear promising, e.g. acrylate groups tethered to the matrix to participate in acrylate-based writing chemistry.

Furthermore, the formula concept can be used to estimate an upper bound on future performance improvements in holographic media. We consider each term in the formula limit expression in turn, starting with the volume fraction of index-contrasting component. The upper bound on this term is evidently 0.5. Next, the index contrast between components has a plausible upper bound at roughly 0.3, since high-index writing monomers have been demonstrated with up to $n \sim 1.7$, and low-index fluorinated organic counter-diffusants have been demonstrated with as low $n \sim 1.4$, constrained in both cases by the requirement of good solubility in the organic matrix. Finally, the usable fraction obviously has an upper bound of 100%.

Thus, an upper bound on achievable $\Delta n$ is given by a hypothetical optimized material with equal volume fractions of two perfectly counter-diffusing components with $n = 1.4$ and $1.7$, yielding a usable $\Delta n$ of $\sim 0.15$. Surprisingly, existing media formulations, with reported $\Delta n$ as high as $0.04$ to $0.05$, are already within a factor of $\sim 3$ of this theoretical upper bound, and thus relatively small future improvements in $\Delta n$ can be expected. This analysis affords a better understanding of the application space for diffusion-driven photopolymers, and highlights the growing importance of design strategies which address other aspects of performance, such as matrix-tethered functional groups for increased spatial and temporal control of photopolymerizations.

## REFERENCES

[1] L. Dhar, A. Hale, H. E. Katz, M. L. Schilling and M. E. Schnoes, "Recording media that exhibit high dynamic range for digital holographic data storage," *Opt. Lett.,* vol. 24, no. 7, pp. 487-489, 1999.

[2] A. Khan, A. E. Daugaard, A. Bayles, S. Koga, Y. Miki, K. Sato, J. Enda, S. Hvilsted, G. D. Stucky and C. J. Hawker, "Dendronized macromonomers for three-dimensional data storage," *Chem. Commun.,* vol. 4, pp. 425-427, 2009.

[3] M. C. Cole, F. R. Askham and W. L. Wilson, "Holographic recording medium with control of photopolymerization and dark reactions". U. S. Patent 13/365,304, 3 February 2012.

[4] D. A. Waldman, R. T. Ingwall, P. K. Dhal, M. G. Horner, E. S. Kolb, H.-Y. S. Li, R. A. Minns and H. G. Schild, "Cationic ring-opening photopolymerization methods for volume hologram recording," *Proc. SPIE,* vol. 2689, 1996.

[5] K. J. Choi, W. M. Chon, M. Gu, N. Malic and R. A. Evans, "Low-Distortion Holographic Data Storage Media Using Free-Radical Ring-Opening Polymerization," *Adv. Func. Mat.,* vol. 19, no. 22, pp. 3560-3566, 2009.

[6] G. Zhao and P. Mouroulis, ""Diffusion Model of Hologram Formation in Dry Photopolymer Materials"," *J. Mod. Opt.,* vol. 41, no. 10, pp. 1929-1939, 1994.

[7] D. J. Lougnot, P. Jost and L. Lavielle, ""Polymers for holographic recording: VI. Some basic ideas for modelling the kinetics of the recording process"," *Pure Appl. Opt.,* vol. 6, no. 2, p. 225, 1997.

[8] D. L. Forman, M. C. Cole and R. R. McLeod, "Radical diffusion limits to photoinhibited superresolution lithography," *Phys. Chem. Chem. Phys.,* vol. 15, no. 36, pp. 14862-14867, 2013.

[9] B. A. Kowalski, A. C. Urness, M.-E. Baylor, M. C. Cole, W. L. Wilson and R. R. McLeod, ""Quantitative modeling of the reaction/diffusion kinetics of two-component diffusive photopolymers."," *Optical Materials Express,* vol. 4, no. 8, pp. 1668-1682, 2014.

[10] M. R. Gleeson, D. Sabol, S. Liu, C. E. Close, J. V. Kelly and J. T. Sheridan, ""Improvement of the spatial frequency response of photopolymer materials by modifying polymer chain length"," *JOSA B,* vol. 25, no. 3, pp. 296-406, 2008.

[11] L. Paraschis, Y. Sugiyama, A. Akella, T. Honda and L. Hesselink, "Properties of compositional volume grating formation with photoinitiated cationic-ring-opening polymerization," in *SPIE's International Symposium on Optical Science, Engineering, and Instrumentation*, 1998.

[12] W. Heller, "Remarks on refractive index mixture rules," *Journal of Physical Chemistry,* vol. 69, no. 4, pp. 1123-1129, 1965.

[13] T. J. Trentler, J. E. Boyd and V. L. Colvin, ""Epoxy resin-photopolymer composites for volume holography"," *Chem. Mat.,* vol. 12, no. 5, pp. 1431-1438, 2000.

[14] S. Mikoshiba, A. Hirao, R. Hayase, K. Matsumoto, N. Sasao and T. Kamikawa, "Holographic recording medium". USA Patent 11/824,029, 29 June 2007.

[15] M.-S. Weiser, T. Rölle, F.-K. Bruder, T. Fäcke and D. Hönel, ""Photopolymer formulations having a low crosslinking density."". US Patent 12/569,224, 2009.

[16] H. Peng, D. P. Nair, B. A. Kowalski, W. Xi, T. Gong, C. Wang, M. Cole, N. Cramer, X. Xie, R. R. McLeod and C. N. Bowman, "High Performance Graded Rainbow Holograms via Two-Stage Sequential Orthogonal Thiol–Click Chemistry," *Macromol.,* vol. 47, no. 7, pp. 2306-2315, 2014.

[17] W. K. Smothers, B. M. Monroe, A. M. Weber and D. E. Keys, ""Photopolymers for holography"," in *In OE/LASE'90, 14-19 Jan, pp. 20-29. International Society for Optics and Photonics*, Los Angeles, CA, 1990.

[18] M. C. Cole and T. J. Trentler, "Thermoplastic holographic media". U. S. Patent 8,071,260, 6 December 2011.

[19] H. Kou, W. Shi, D. J. Lougnot, Y. Lu and H. Ming, "Dendritic polyisophthalate endcapped with naphthyl groups for holographic recording," *Polym. Adv. Tech.,* vol. 15, no. 9, pp. 508-513, 2004.

[20] M. Ayres, K. Anderson, F. Askham and B. Sissom, "Progress in second-generation holographic data storage," *SPIE Optical Engineering+ Applications,* p. 92010V, 2014.

[21] H. Berneth, F.-K. Bruder, T. Fäcke, R. Hagen, D. Hönel, D. Jurbergs, T. Rölle and M.-S. Weiser, "Holographic recording aspects of high-resolution Bayfol® HX photopolymer," *Proc. SPIE,* vol. 7957, 2011.

[22] B. M. Monroe, W. K. Smothers, D. E. Keys, R. R. Krebs, D. J. Mickish, A. F. Harrington, S. R. Schicke, M. K. Armstrong, D. M. Chan and C. I. Weathers, "Improved photopolymers for holographic recording. I, Imaging properties," *J. Imaging Sci.,* vol. 35, no. 1, pp. 19-25, 1991.

[23] R. T. Ingwall and M. Troll, "Mechanism of hologram formation in DMP-128 photopolymer," *Opt. Eng.,* vol. 28, no. 6, p. 286586, 1989.

[24] R. T. Ingwall, A. Stuck and W. T. Vetterling, "Diffraction properties of holograms recorded in DMP-128," *OE/LASE'86 Symp (January 1986, Los Angeles), International Society for Optics and Photonics,* pp. 81-87, 1986.

[25] A. Beléndez, A. Fimia, L. Carretero and F. Mateo, "Self-induced phase gratings due to the inhomogeneous structure of acrylamide photopolymer systems used as holographic recording materials," *Appl. Phys. Lett.,* vol. 67, no. 26, pp. 3856-3858, 1995.

[26] M. Cole and M. Ayres, "Latent holographic media and method". US Patent 11/333,527, 18 January 2006.

[27] D. A. Waldman, H. Li and M. G. Horner, "Volume shrinkage in slant fringe gratings of a cationic ring-opening holographic recording material," *J. Imaging Sci. Tech.,* vol. 41, no. 5, pp. 497-514, 1997.

[28] T. Todorov, P. Markovski, N. Tomova, V. Dragostinova and K. Stoyanova, ""Photopolymers—holographic investigations, mechanism of recording and applications"," *Optical and Quantum Electronics,* vol. 16, no. 6, pp. 471-476, 1984.

[29] V. L. Colvin, R. G. Larson, A. L. Harris and M. L. Schilling, ""Quantitative model of volume hologram formation in photopolymers"," *J. Appl. Phys.,* vol. 81, no. 9, pp. 5913-5923, 1997.