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Comment on C.E. Close, M.R. Gleeson and J.T. Sheridan "Monomer Diffusion Rates in Photopolymer Material Part 1. Low Spatial Frequency Holographic Gratings

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Comment on C. E. Close, M. R. Gleeson and J. T. Sheridan “Monomer diffusion rates in photopolymer material. Part I. Low spatial frequency holographic gratings” J. Opt. Soc. Am. B / Vol. 28, No. 4 / April 2011 pp 658- 666 [1]

Abstract: We examine the statements in [1] that a “confusingly wide range of values (of monomer diffusion rates) have been reported in the literature” and that the authors “provide unambiguous evidence that the monomer diffusion rate in a commonly used acrylamide polyvinyl alcohol- based material is of the order of 10^{-10} cm²/s”. We discuss this result and briefly summarize the differences between two models which have been proposed to explain behaviour of holographic photopolymers and consider their implications.

The authors of [1] provide some examples of “confusion” as follows. “Results involving studies using acrylamide/polyvinyl alcohol (AA/PVA), reported by a number of independent research groups, have provided a wide range of diffusion values, estimated using a number of methods [19,20]. Significantly, many of these disagree by factors of ~1000 from the values predicted by the non-local polymerization-driven diffusion (NPDD) model. Toal et al. [19,20], using AA/PVA layers of different thicknesses, estimated the rate of AA diffusion D_{AA} to be 10^{-7} – 10^{-8} cm²/s, while Gallego et al. estimated a diffusion constant value of $\sim 10^{-8}$ cm²/s [21,22]”.

The authors of [19,20] in [1] are members of a single research group, not “a number of independent research groups”. The range of values which they report covers just one order of magnitude although measured under different experimental conditions. Furthermore the value of diffusion rate reported in Gallego *et al.*, [21,22] in [1], does not disagree with [19,20] in [1] although the disparity between all of these data and the predictions of NPDD is certainly noteworthy.

Confusion is created in the next paragraph of [1], which states that “Lawrence et al. [14], applying an early version of the NPDD in 2001, estimated values of $D_{AA} \sim 10^{-14}$ cm²/s.” Later in the same paragraph Lawrence et al. [14] becomes Sheridan et al. [14] but now claiming consistency with [15,16] in [1] in estimating a value of the order of 10^{-10} cm²/s.

The new results in [1] range over more than two orders of magnitude from $3.19 \cdot 10^{-7} \pm 2.53 \cdot 10^{-7}$ cm²/s to $5.64 \cdot 10^{-10} \pm 5.13 \cdot 10^{-10}$ cm²/s, and encompass the range reported in [19-22] in [1]. The data reported in [1] were obtained under differing experimental conditions of temperature and humidity and demonstrate that a wide range of diffusion rates may be obtained in the same photopolymer composition in a single laboratory.

Diffusion rates are important in both the two-way diffusion model [2-4] and in the NPDD model [5]. The latter assumes that polymer chains grow away from their initiation point, resulting in smearing of the recorded profile. Such a process will indeed dominate under conditions of comparatively slow diffusion. The model predicts that improvement in high spatial frequency response can be achieved by creating shorter polymer chains during holographic recording [6]. Despite the successful theoretical

modeling no experimental evidence for improvement of acrylamide-based photopolymer response at spatial frequency higher than 3000 lines/mm by adopting this approach has so far been reported.

On the other hand the two-way diffusion model [2-4] assumes that during holographic recording short terminated and unterminated polymer chains diffuse away from the bright fringes thus reducing the refractive index modulation. Such processes will dominate under conditions of comparatively fast diffusion and help to explain the decrease in diffraction efficiency at high spatial frequencies at which the fringe spacing is small and there is enough time for some of the polymer chains to escape from the bright fringes, before the medium becomes less permeable due to complete polymerization. The model [4] predicts that high spatial frequency response of such systems may be improved by decreasing the permeability of the photopolymer matrix and by avoiding the creation of readily diffusing short polymer chains. The model has enabled the optimization of the high spatial frequency response of the materials, to the extent that full colour reflection holography [7] is now well established, along with a range of colour changing holographic sensors [8,9].

Diffusion of short polymer chains and non-local polymerisation processes may both contribute to limited spatial resolution in these materials. One or the other may dominate depending on the permeability of the recording material and the exposure conditions.

We would add the following remarks.

Study of the photopolymer system referred to in the abstract of [1] began at the Dublin Institute of Technology (DIT), in 1988. The facts relating to its development may be briefly stated. Calixto [10], in a succinct review of progress in the development of holographic photopolymers, reported a dry red-sensitive photopolymer layer, which became the basis of studies by Martin and Toal [11-12] at DIT, and Martin *et al.* [13,14] who optimized the composition of the material for use at 514 nm and improved its stability. Martin also offered a diffusion based explanation for the reduction in diffraction efficiency with increasing spatial frequency [15] and dye diffusion rates were measured by Feely [16]. Naydenova *et al.* [2] obtained values of diffusion rates in the short exposure regime, in detailed studies aimed at identifying the physical processes in holographic recording, a vital step in developing the principles of photopolymer system design for holographic applications. Two distinct diffusion processes were identified and these were discussed further by Martin *et al.* [3] and incorporated in the two-way diffusion mathematical model by Babeva *et al.* [4].

The lack of any reference to the origin and development [10-16] of the “commonly used acrylamide based photopolymer” [1] is somewhat misleading. The impression is given that the authors of [32-34] in [1] are the originators. This is not correct as the foregoing makes clear.

Close *et al.* [1] concludes with the statement that “It has been brought to our attention that, in a recent paper by Toal *et al.* [55], inappropriate initial monomer and polymer diffusion values have been employed to discuss a similar (*sic*) AA/PVA-type material.” This claim, whether by the authors themselves or by anonymous third parties, is presented without justification or evidence and has no place in a scientific paper.

The authors of [1] refer to each of [19,20,30 and 55] in [1], as Toal *et al.* These are, respectively, Naydenova *et al.*, Babeva *et al.*, Babeva *et al.* and Babeva *et al.* While some internal consistency is adopted in citing these particular references, the format differs from that used for all other references cited by name.

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