

Monomer diffusion rates in photopolymer material: Part I. Low spatial frequency holographic gratings: reply

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In [1,2] an error (by a factor of 1000) in the diffusion rate of monomer in a photopolymer material used by the authors of [3], is presented. In [3] no errors are identified in our analysis and our physical evidence is not addressed. It is implied that our model and our results are disproven by the results in the papers referenced in [3]. In fact these papers do not provide any such quantitative evidence. The observations made regarding the significance of the authors' contributions, in particular the validity of their model and the practical importance of their material are also discussed. © 2012 Optical Society of America

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1. REPLY

In our two part paper [1,2] we demonstrate that an error has been made by Toal *et al.* [3,4] in relation to their interpretation of their experimental results for their acrylamide/polyvinyl alcohol (AA/PVA) photopolymer material. We show that their value for the rate of monomer diffusion in their AA/PVA, 10^{-7} cm²/s, is incorrect by a factor of 1000. Our estimated value, of 10^{-10} cm²/s, agrees with typical values found using the nonlocal photo-polymerisation driven diffusion model, (NPDD). In the second part of our paper we place their diffusion value within the context of other materials. These results are neglected in [3].

Despite the large size and the serious consequences of the error identified in [1,2], the authors of [3] have chosen not to report on their attempts to repeat our analysis so as to quantitatively disprove our results. Instead in relation to our results, Toal *et al.* [3] first state that our values encompass theirs. Then they imply that the differences may arise due to differences in the material composition. Finally they state that our material composition is in fact identical to theirs and that we have given the false impression that we developed this material. Most of the actual text in [3] however involves a long listing of their papers, all of which contain interpretations of the material behavior that our paper [1,2] proves are physically inconsistent. Let us begin by providing further evidence, (besides the contents of [1,2]), to demonstrate that their model and results do not in fact quantitatively contradict our results. Toal *et al.* claim that the development of their model began in the early 1990s (see Reference 15 in [3]). Recently, in 2010, they compare their experimental results and the predictions of their model (see Figures 6 and 7 appearing in Reference 4 in [3]) and state that: “*The good agreement regarding the shapes and slopes of the curves can be easily seen, but the calculated values of Δn are again higher than the measured ones.*” In fact a cursory examination of these

figures demonstrates that the predictions of their model and their experimental results disagree significantly in shape and by unexplained factors of between 6 (Figure 6) and 40 (Figure 7). Such disagreements, of between 500% and 3900%, (following >15 years of model development), do not indicate an accurate physical understanding of the material behavior. Furthermore such differences cannot be simply explained away by arbitrarily changing the values of the component refractive indices. We note that the NPDD model, introduced by Sheridan *et al.* in 2000 [5], (see [6–8]), does not suffer from any such quantitative uncertainty. When using the NPDD model, accurately measured component refractive index values are used, see [9], in agreement with tabulated values from the general literature. The NPDD model permits the inhibition, short exposure and postexposure effects to be quantitatively predicted. Most significantly in relation to [3], these quantitative results support the value of monomer diffusion reported in [1,2]. While several other papers are cited in [3] to support the authors' claims, we must emphasize that none of these papers contain any accurate quantitative comparison between, for example, the spatial frequency responses of a material optimized using the predictions of their model and that of an unmodified material. Such detailed reproducible evidence has been repeatedly and consistently supplied using the NPDD model (see [7–8] and the references therein).

As noted in the abstract the authors of [3] identify no scientific errors, either in the models used in [1,2] (optical or material), or with any of the experimental results presented in [1,2]. In fact in [3] the authors seem to imply that our results may be correct for our material (i.e., binder weight etc.), but that for their material, or possibly due to unexplained differences in laboratory conditions, large differences are possible. No supporting evidence for these claims is supplied, e.g., their different plasticizer concentration value. No results

demonstrating the effects of changes in the specific concentrations they mention in [3] on the rate of monomer diffusion are made available. If such random variations occur, this would undermine any claim to be able to generate a stable material.

We now deal with the remaining issues raised in [3].

Estimates of the rate of monomer diffusion made by four independent research groups are presented in [1,2]. Ranked in cm^2/s , these are: (i) 10^{-7} , (ii) 10^{-8} , (iii) 10^{-10} , and (iv) 10^{-14} . In all cases references are supplied, see [1,2], however the authors of [3] seem confused and unwilling to accept that these independent results range three orders of magnitude above and below the correct range of values, i.e., $\sim 10^{-10} \text{ cm}^2/\text{s}$. They also seem confused by our referencing [4].

Toal *et al.* [3] mistakenly imply that we estimate a value of monomer diffusion of $10^{-7} \text{ cm}^2/\text{s}$ and that our results “encompass their range of values.” As indicated in [1,2] we purposely perform an uncoveredplated (incorrect) and a coveredplated (correct) data analyses. While the uncoveredplated case analysis gives an incorrect highest value of $\sim 10^{-7} \text{ cm}^2/\text{s}$, the coveredplated case analysis gives a fastest possible limiting value of monomer diffusion of $10^{-9} \text{ cm}^2/\text{s}$. We explain why this limiting value is too high and also experimentally confirm that the slowest possible value is $10^{-11} \text{ cm}^2/\text{s}$ [1,2]. This maximum value, of $10^{-9} \text{ cm}^2/\text{s}$, is one of the core results presented in [1,2]. The individual value ranges listed in [3] are large, (as explained in [1,2]), as in these cases coverplating was on purpose not used. Coverplating, as is confirmed in [1,2], significantly increases the precision of the value obtained.

Toal *et al.* appear to accept in [3] that the nonlocal effect arising due to chain growth takes place in their material. However they imply that a completely separate model (their model) is necessary for: (i) materials which have their higher rates of diffusion and (ii) for gratings recorded above a certain spatial frequency (i.e., above 3000 1/mm). No evidence in support of these claims is supplied, e.g., a simulation demonstrating the breakdown of their model proving the necessity for the NPDD model at lower rates of diffusion. To our knowledge the NPDD model has already been applied to characterize five fundamentally different types of dry photopolymer layer materials: (1) green and red sensitized AA/PVA, (2) Dupont OmniDex photopolymer, (3) Trentler *et al.* (Irgacure sensitized two step epoxy resin based), (4) Phenanthrenequinone/poly methyl methacrylate (PQ/PMMA), and (5) a photopolymer system developed by Bayer MaterialScience. It seems peculiar to imply that AA/PVA alone requires two different models, involving two diffusion rates differing by three orders of magnitude.

In [3] Toal *et al.* mistakenly claim that control of the material spatial frequency response using the NPDD model has only been experimentally verified for spatial frequencies less than 3000 lines/mm. This comment appears to refer to results presented in [7] in which, while maintaining the rate of polymerisation, we demonstrated chain shortening using a chain transfer agent (CTA). In this way we verified the NPDD prediction by quantifying the associated decrease in the nonlocal effect and demonstrating an improved material spatial frequency response up to ~ 3000 lines/mm. While no errors in [7] are indicated by Toal *et al.*, they imply that only their model is verifiable at higher spatial frequencies. In fact the results in [7] have been extended, in [10,8], to include reflection geome-

try gratings, (which we first studied in 2001, [11]), for spatial frequencies up to ~ 4800 lines/mm. Furthermore, the predictions of the NPDD model for spatial frequencies up to 5000 1/mm in a Bayer MaterialScience material have been confirmed, [12], and a detailed comparison of the spatial frequency performance of the Bayer material with the equivalent results in AA/PVA is presented [13]. These results all support the treatment of diffusion reported in [1,2].

We urge the editor to include the full comment as requested by Toal *et al.* in [3].

Many claims are made in [3] and in the listed references regarding the significance of the authors contribution. In a detailed review of photopolymer materials [14] published in 2001 we highlighted their contribution (i.e., their experimental studies involving the introduction of a green sensitizing dye into a previously developed red sensitised AA/PVA material). The review [14] is inclusive (containing ~ 69 references) and has been widely referenced in the literature. Clearly the authors of [3] are familiar with [14] and have not raised any objections to the contents. Toal *et al.* cannot therefore be concerned that we have not explicitly acknowledged their contribution in print. They also supply no reasonable explanation for their confused false impression that we have implied in [1,2] that their contribution was made by us. They do however appear extremely concerned that we have not referenced them enough in [1,2]. Given the extremely serious nature of the quantitative errors identified by us in their papers we believe we have referenced their work appropriately. Finally given the scale of the error identified in [1,2] the focus of their concerns in [3] seems misplaced.

Returning to their claims to have understood and optimized their green sensitised AA/PVA material, as noted these claims are not supported by the contents of their reference list in [3]. They have published no quantitative study regarding the properties of their dye in their material, (i.e., explaining the related inhibition effects, photo-sensitizer regeneration, the kinetics of intersystem crossing, and bleaching effects). We have published such detailed quantitative studies (see [15,16] and references therein). It is critically important to perform reproducible quantitative dye studies in order that polymer initiation can be characterized and accurately modeled. Without such detailed knowledge no quantifiable optimisation process can in fact be attempted or realized.

The significance of their contribution must also be judged in the context of the actual practical importance of their AA/PVA material and the consistency of their results. They have repeatedly claimed that AA/PVA has excellent properties. One of the most fundamentally important of these is layer stability. In 1997 (Reference 14 in [3]) the authors mistakenly claim that the material suffers no shrinkage during recording. In 2004 (Reference 2 in [3]) they appear to withdraw this statement claiming instead that the material suffers negligible shrinkage during and after the holographic recording compared to other unspecified material systems. In this same paper they however go on to imply that their material will have excellent performance, because of their high rate of diffusion, compared to commercial DuPont OmniDex photopolymer. Most recently, in 2011 [17], the authors appear to agree with our conclusions, in 2001 [11], 2005 [18] and in [1,2], that appreciable shrinkage and swelling does take place in their material and they imply that only significant modification of the material composition,

(i.e. the inclusion of nanoparticles), may allow it to be stabilized. Clearly AA/PVA does not in fact perform sufficiently well to be considered even a precommercial grade material. It has many serious drawbacks including: (i) poor environmental stability and low glass transition temperature; (ii) toxic components; (iii) significant shrinkages/swelling during and postexposure; (iv) postexposure effects leading to a significant reduction in grating strength, (an absence of dark amplification), and (v) poor spatial frequency response. In a recent publication, (see Reference 7 in [3]), Toal *et al.* state that their results strongly confirm that their latest material can be employed in future commercial holographic applications. Despite this claim Toal *et al.* do not cite any commercially available products based, for example, on the many well established sensing results detailed in [3]. This is perhaps not surprising given that they also do not bring to our attention the results of any quantitative studies involving large scale commercial material production (e.g., uniformity, packaging, lifetime etc.). These facts, combined with the results in [1,2], make their claims appear somewhat premature.

The comment [3] ends with the curious claim that it is unacceptable for us to reprint the value of monomer diffusion given in their paper (see Reference 55 in [1]), i.e., 10^{-7} cm²/s, and to state this value is inappropriate. As shown in [1,2] his value is inappropriate by a factor of 1000.

2. CONCLUSIONS

In their comment Toal *et al.* identify no errors in our analysis [1,2]. They also provide no scientific quantitative evidence contradicting our results. Instead they list their papers, which repeat their incorrect qualitative interpretations of their results. Our correct diffusion value, presented in [1,2], and the large discrepancies, of up to 3900%, in their published results clearly call into question their claims to have understood, modeled and optimized their AA/PVA material. Using the NPDD model we have dealt in a credible quantitative manner with the physical implications of the correct monomer diffusion value presented in [1,2] and with the resulting practical consequences [7–8,13]. Despite the serious limitations of the AA/PVA material we consider it of academic value, in particular because it is relatively inexpensive and simple to use.

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