

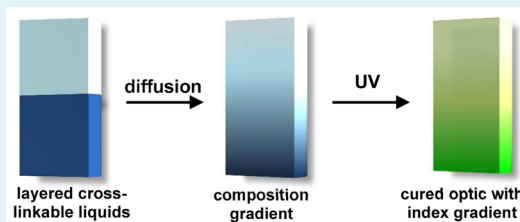
Gradient-Index Materials Based on Thiol–Ene Networks

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S Supporting Information

ABSTRACT: Gradient-index (GRIN) optics offer spatially varied refractive indexes that can enhance current imaging technologies. Current methods to fabricate GRIN optics are highly complex and costly. Here we report a simple and efficient method that utilizes commercially available reagents to fabricate polymeric GRIN optics with significant refractive index differences ($\Delta n = 0.04$). First, two different mixtures of network precursors are layered and time allotted for molecular diffusion in the liquid state, prior to curing. The resulting, partially mixed layers are UV-cured to yield clear, glassy molecular networks with fixed refractive index gradients. The fully cured network resins exhibit smoothly varying composition and refractive index over centimeter length scales, confirmed by spectroscopy and interferometry.

KEYWORDS: gradient materials, thiol–ene click reaction, controlled diffusion, photopolymerization



INTRODUCTION

Optical elements form the core of many technologies accomplishing image formation, light collection, and light projection. However, traditional elements are limited by geometry and a constant refractive index, and they often dominate a system's weight and cost. A gradient-index (GRIN) optic has a spatially variant refractive index, allowing light to follow curved trajectories. GRIN lenses are modernizing optical devices by reducing their size, weight, number of elements, and cost. While the GRIN concept was first suggested in the mid-19th century,¹ only in the last few decades have GRIN lenses with large overall index changes ($\Delta n > 0.04$) and depth of gradient ($d > 20$ mm) emerged. Control of refractive index gradients over large dimensions (centimeters), in addition to the ability to prepare GRIN lenslet arrays and coatings,² is advancing optics for communications, imaging and display systems, sensing,³ solar concentrators,^{4,5} and biomedical technologies.⁶

Compared to their inorganic counterparts,^{7,8} polymeric GRIN optics can exhibit a high variation of refractive index ($\Delta n \sim 0.1$), exceeding that of quartz-derived glasses. Polymer-based GRIN optics are appealing due to their low density, shatter resistance, flexibility, tunable mechanical properties, and mild synthesis conditions.⁹ Gradient-index polymers have been fabricated by a variety of methods including interfacial gel copolymerization,^{3,10} copolymerization involving immersion,¹¹ photopolymerization,^{12,13} and layer-by-layer extrusion into a stack of thin films.^{14–17} While these approaches have been successful in various geometries, they are process-intensive and require precisely controlled conditions and handling to avoid defects caused by, for example, stress-induced birefringence or phase separation. The development of lightweight materials with improved optical loss characteristics and tunable index of

refraction and Abbe number, a measure of a material's optical dispersion, is critical to expanding the design space of GRIN optics.

The highly efficient, click nature of thiol–ene reactions is especially attractive for fabricating optical components, including GRIN lenses.^{18,19} Liquid precursors containing multifunctional thiol and ene functional groups can be rapidly transformed into highly uniform, cross-linked polymer networks by UV-irradiation under ambient conditions. We have recently demonstrated spatial-temporal control of mass transport within such well-defined thiol–ene networks via photo-induced diffusion.²⁰ The thiol–ene reaction proceeds rapidly to high yield without the formation of side-products. Depending on the monomer type and functionality, air-cured materials can exhibit mechanical properties ranging from low modulus elastic materials to hard materials capable of sustaining high impact without cracking or fracture. Further, because of the incorporation of highly polarizable sulfur atoms, these networks exhibit relatively high refractive indices ranging from 1.491 to 1.703 with correspondingly high Abbe numbers between 24.3 and 45.0.^{21,22} Their exceptional transparency, scratch resistance, and tunable hardness make them ideal for many optical applications.²¹

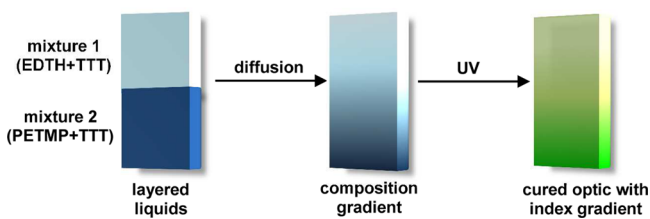
Here we present a simple and inexpensive method involving photoactivated covalent bond formation to fix-in high quality optical gradients. Our approach is illustrated in Scheme 1. By allowing two sets of chemically distinct, but miscible, thiol–ene precursors to diffuse as liquids, a smooth composition gradient can be formed. Following rapid photo-cross-linking by UV

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Scheme 1. Approach to Achieving Index Gradients Derived from Molecular Diffusion of Thiol–Ene Resin Precursors Followed by UV-Fixation



irradiation, a stable and transparent solid with optical and mechanical gradients can be generated.

EXPERIMENTAL SECTION

Materials. 1,2-Ethane dithiol (EDTH), 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H, 3H, 5H)-trione (TTT), and 2,2-dimethoxy-2-phenylacetophenone (DMPA) were purchased from Sigma-Aldrich. Pentaerythritol tetrakis(3-mercaptoproionate) (PETMP) was bought from VWR International LLC. All chemicals were used as received. Structures of all the used thiols and ene are shown in Figure 1.

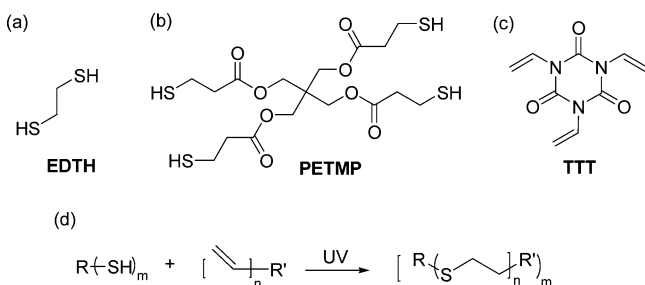


Figure 1. Thiol–ene resin precursors: (a) 1,2-ethane dithiol (EDTH), (b) pentaerythritol tetrakis(3-mercaptoproionate) (PETMP), (c) 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H, 3H, 5H)-trione (TTT), and (d) UV-initiated cross-linking reaction between multifunctional thiol and ene.

Network Synthesis. EDTH-TTT and PETMP-TTT mixtures were stoichiometrically mixed in different vial containers, each with 1 wt % DMPA added (compared with total weight). Caution was taken to protect the mixtures from any sources of light during mixing. The container in which the material is photochemically cured was made by clamping two quartz glasses and a (1.200 mm thick) rubber spacer in between. To make a typical homogeneous sample, EDTH-TTT and PETMP-TTT were mixed with specified volumetric ratio and rigorously stirred until homogeneous. For a typical diffusion sample (GRIN), EDTH-TTT and PETMP-TTT were layered in an unmixed way in the mold. Then, the sample was covered with aluminum foil and was allowed to diffuse in room temperature for specified time. The dimension of the cured sample was 40 mm × 10 mm × 1.2 mm, with diffusion occurring along the long dimension.

GRIN Fabrication. Photocuring of all samples was conducted with a UV lamp (Oriol Arc Lamp Supply 66002, Oriol Corp.). The UV beam directed to the samples was first scattered using a piece of crumpled aluminum to more uniformly irradiate the sample during curing. Before curing, the UV lamp was adjusted so that the intensity of the directed beam at 325 nm was 2.0 mW/cm². The samples were placed in a box covered with aluminum foil on the inside to maximize the area in contact with the beam. For every 5 min of UV cure, the sample was flipped to the other side to achieve uniform curing. Typically, pure EDTH-TTT samples required at least 40 min of curing while pure PETMP-TTT samples required only 15 min of curing. The curing time for homogeneous samples ranged between 15 and 40 min, depending on the volumetric ratio of EDTH-TTT and PETMP-TTT.

For diffusion samples, the curing time depends solely on the time required for the EDTH-TTT sample to achieve a glassy state. After UV cure, the samples were placed in a 60 °C oven overnight as a postcure. Attenuated total reflection-Fourier transform-infrared (ATR-FT-IR) measurements were applied to confirm almost all the monomers (>98%) have been consumed during the curing process.

GRIN Characterization. ATR-FT-IR spectroscopy (Shimadzu 8000S) was used to assess the presence of a specific peak from a characteristic functional group near the sample surface. Index measurements of homogeneous samples were made on a Pulfrich refractometer (wavelength 632.8 (HeNe) or 532 nm, index accuracy from 0.0002 to 0.001), while the nondestructive refractive index (RI) profile is obtained with a customized beam deflection system (wavelength 632.8 nm, index accuracy from 0.0001 to 0.001).

RESULTS AND DISCUSSION

The thiol–ene resin precursors in Figure 1 were chosen for this study based on their optical characteristics, miscibility, and commercial availability. Networks formed from these precursors appear as optically clear resins and occupy the high end of the polymer RI range.^{21,22} Their exceptional transparency, hardness, and capability to be polished into optical-quality monoliths make them suitable for most optical applications. Moreover, all three resin precursors are miscible over their entire composition range, allowing controlled molecular diffusion while avoiding phase separation.

Homogeneous thiol–ene resins were mixed and cured to confirm the relationship between refractive index and composition. For example, a 3:2 stoichiometric mixture of EDTH and TTT with 1 wt % photoinitiator (2,2-dimethoxy-2-phenylacetophenone, DMPA) was cured under 325 nm UV light resulting in a rubber-like cross-linked network (Young's modulus $E = 17$ MPa) with a refractive index of 1.60 at 632.8 nm at room temperature. Identical UV-curing of a 3:4 stoichiometric mixture PETMP and TTT leads to a much stiffer material ($E = 1570$ MPa) with a refractive index of 1.56 at 632.8 nm. Homogeneous optics with intermediate refractive indices could be fabricated by mixing different volumes of the two thiol–ene mixtures followed by UV curing. The refractive index and the composition formed a linear relationship as seen in Figure 2. Higher refractive indices were observed with increasing EDTH-TTT content in the formulation. This

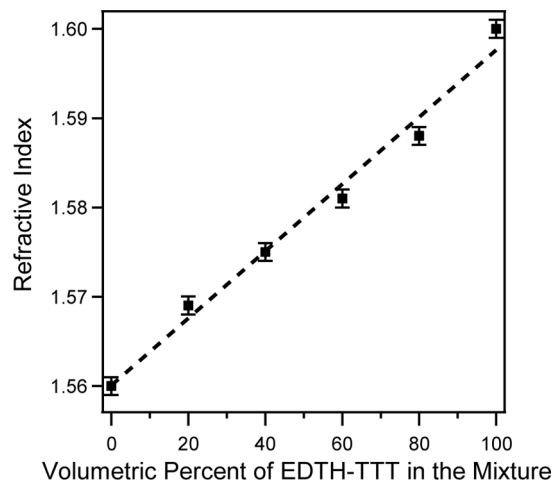


Figure 2. Refractive index versus composition of homogeneous thiol–ene networks. Error bars reflect experimental uncertainty of ± 0.001 from refractometry. The dashed line is a linear least-squares fit to the data.

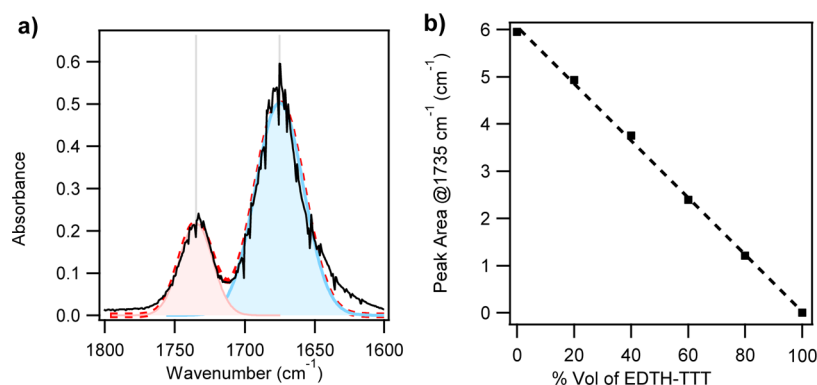


Figure 3. Determination of network composition from FT-IR: (a) FT-IR peak deconvolution of sample containing 20% of EDTH-TTT (black line, original data; pink and blue area, deconvoluted peaks; red dashed line, fitted curve). (b) Plot of FT-IR peak area of PETMP carbonyl absorbance versus composition of homogeneous thiol-ene resins. The dashed line is a linear least-squares fit to the data.

relationship validates that the chosen thiol-ene precursors are qualified candidates for GRIN optics fabrication following Scheme 1.

The composition of homogeneous resins was quantified using FT-IR analysis. The FT-IR spectrum of the pure PETMP-TTT sample reveals a well-resolved absorption from PETMP's ester carbonyl at about 1735 cm^{-1} , which is not observed in the spectrum of pure EDTH-TTT. Both homogeneous samples exhibited a distinct absorption band at about 1675 cm^{-1} due to carbonyl stretching of TTT's triazine ring that was comparable in intensity to PETMP's carbonyl absorption. For samples exhibiting both peaks, peak deconvolution (Figure 3a) was accomplished by fitting FT-IR absorbances with three-parameter Gaussian functions (adjustable peak position, height, and width). Composition was then determined by integrating the Gaussian peaks, with the assumption that both carbonyl stretches have the same extinction coefficients. As expected, for the cured resin mixtures, the integrated peak intensity from the PETMP ester carbonyl stretch decreases linearly as the EDTH-TTT volumetric ratio increased (Figure 3b).

To fabricate gradient networks, two uncured stoichiometric resins with different refractive indices were carefully layered into a quartz mold. The two precursor mixtures, while completely miscible, were carefully added and remained in two unmixed layers, with a well-defined interface due to the presence of the viscous (PETMP-TTT) component. Diffusion was allowed at room temperature, and the interface remained faintly visible after about 20 h, although it traveled about 4.0 mm toward the EDTH-TTT side. After a specified time (1 h, 1 day, 3 days, and 7 days), the composition gradient was fixed by photoinduced thiol-ene cross-linking. The sample cured following a diffusion time of 1 h displayed a clear interface (Figure 4), and samples cured following longer diffusion times were free of interface or layering of any kind, confirming that diffusion had alleviated much of the compositional contrast.

The evolution of composition profiles with diffusion time was quantified by conducting surface analysis of cured films. Figure 5a,b shows excerpts of ATR-FT-IR spectra acquired at different film positions, in the direction of diffusion, for films fabricated with 1 h and 7 day diffusion times. The integrated peak intensity of PETMP's ester peak at 1735 cm^{-1} is a quantitative measure of PETMP's concentration in the cured resin. Both samples in Figure 4 display comparable absorbance at the PETMP end since there, the ester carbonyls were unaffected by diffusion. This region remains pure PETMP-TTT

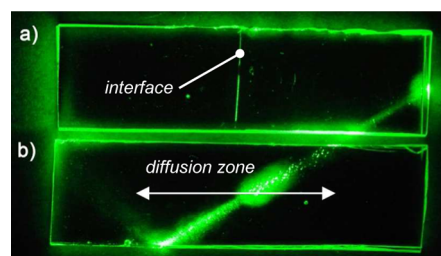


Figure 4. Images of thiol-ene resins cured after (a) 1 h of diffusion time and (b) 7 days of diffusion time. Green laser light was used to illuminate the sample, and an interface between the two formulations is apparent in part but not in part b. Specimens have dimensions of $40\text{ mm} \times 10\text{ mm} \times 1.2\text{ mm}$ and are viewed through their 1.2 mm thickness.

throughout the diffusion time. Similarly, the PETMP peak was absent from the EDTH side through entire diffusion time, indicating the opposite end is unaffected by diffusion as well. The sample cured after 1 h of diffusion exhibits an abrupt change in absorption characteristics (Figure 5a) at the same location that an optical interface is present. This indicates a steep composition gradient around the contact area between the two layers. On the other hand, the resin that allowed a 7-day diffusion time appeared optically clear and showed a gradual decrease in the PETMP peak intensity from the PETMP-TTT side to the EDTH-TTT side (Figure 5b). The integrated peak intensity of PETMP's carbonyl is plotted against distance in Figure 5c. The data for resins with 1 h and 7-day diffusion times agree at the two extremes (0 and 40 mm). The sample with a 7-day diffusion time exhibited a nearly linear composition change over a distance of about 2.5 cm.

The spatial variation of refractive index in the cured resins was assessed using laser beam deflection.²³ Figure 6 shows profiles of resins with different diffusion times. All samples showed the same magnitude of refractive index change $\Delta n = 0.04$, which agrees with the index contrast between the two homogeneous resins: $n_1 - n_2 = 1.60 - 1.56 = 0.04$. Similar to the composition profile deduced from Figure 5c, the refractive index profile of the resin with a 1 h diffusion time displayed an abrupt, discontinuous change. With increasing diffusion time, a gradual smoothing of the transition region is apparent and the slope (dn/dx) becomes more uniform. After 7 days, the index varied nearly linearly with position, and an index contrast of 0.04 over 2.5 cm was achieved; and this demonstrates the feasibility of this approach to prepare well-defined GRIN optics.

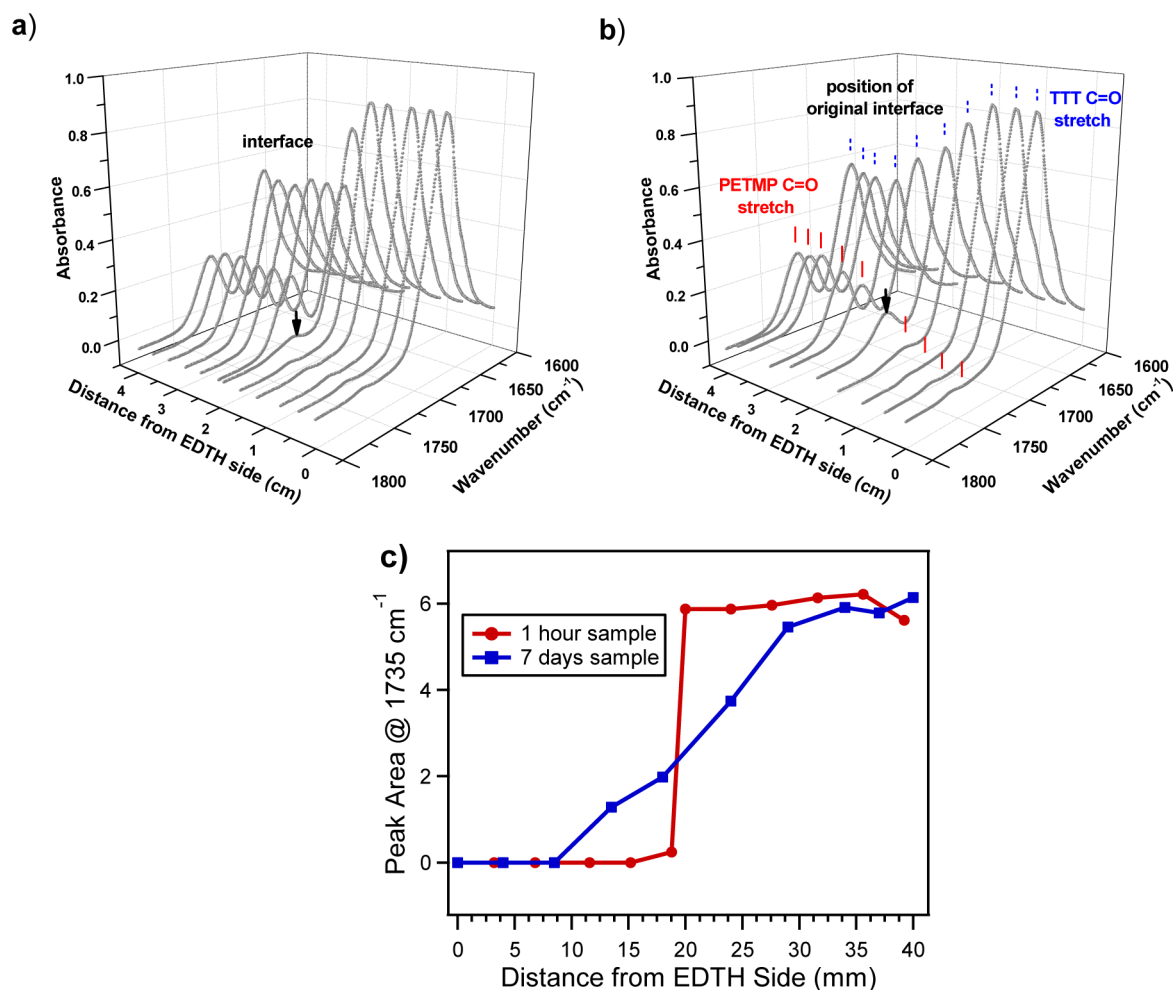


Figure 5. Composition analysis following room temperature diffusion (EDTH-TTT | PETMP-TTT) and curing of thiol–ene precursors. FT-IR spectra are displayed at different positions along the specimen’s diffusion direction following (a) curing after 1 h of diffusion and (b) curing after 7 days of diffusion. Pane c shows the integrated peak intensity of PETMP’s ester C=O stretch for both of these samples.

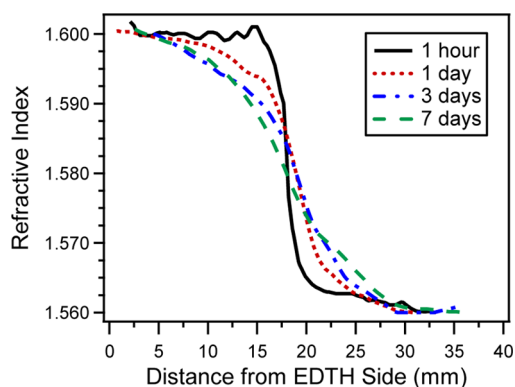


Figure 6. Refractive index profiles along the diffusion axis of thiol–ene gradient samples (EDTH-TTT | PETMP-TTT) cured after different diffusion periods at room temperature.

In this sample, molecular diffusion occurred over a distance ~ 10 mm in 7 days, and based on that time interval, the effective diffusion coefficient of monomers through the liquid mixtures could be estimated as $D \sim (2Dt)^{1/2} = 0.8 \times 10^{-6} \text{ cm}^2/\text{s}$. This value is somewhat smaller than the typical diffusion coefficients of small molecules through liquids ($10^{-5} \text{ cm}^2/\text{s}$);²⁴ however, this is not surprising since PETMP-TTT is a highly viscous

liquid. Furthermore, some polymerization likely occurred over a long period (7 days), even without UV irradiation, slowing the rate of mass transfer. After 7 days of diffusion, the shape of the refractive index profile (Figure 6) matched the shape of the composition profile (Figure 5c) but not precisely; the maximum deviation was $\sim 5\text{--}10\%$. This discrepancy is not unexpected because (i) the refractive index is not precisely correlated to composition, as evidenced in Figure 2; (ii) the monomer stoichiometry in the diffusion zone is not perfectly balanced. Interferometry was performed on the sample prepared with a 7-day diffusion time to give a visible depiction of the refractive index distribution over the material. These data are provided as Supporting Information.

In addition to a refractive index gradient, the diffusion-reaction technique described here should be capable of creating gradients in mechanical properties. The Young’s modulus was measured for the two limiting formulations, EDTH-TTT and PETMP-TTT, and was 2 orders of magnitude apart (17 and 1570 MPa, respectively). A compositional gradient should impose a gradient in stiffness between these two values. McNair and co-workers demonstrated tunable mechanical properties and glass transition temperatures of ternary thiol–ene mixtures.²⁵

CONCLUSION

In summary, we have shown that diffusion of thiol–ene precursors followed by photoinduced cross-linking is a straightforward approach to form GRIN resins. Thiol–ene networks are well suited for optics because they exhibit low intrinsic stress and minimal birefringence upon curing, and they can display low optical loss. Careful selection of thiol–ene precursors could lead to advanced GRIN optics with tailorable index and Abbe number characteristics. Moreover, the ability to use light to spatially control polymerization or network functionalization is unique and could lead to light-writable GRIN optics. By utilizing other suitable photomonomers to impart varying chemical, mechanical, optical, or even biological properties, this diffusion-reaction approach potentially represents a new pathway to novel gradient polymers.

ASSOCIATED CONTENT

Supporting Information

Interferometry figure and comments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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