Dual-Function Enhancer for Near-Infrared Photopolymerization: Kinetic Modeling for Improved Efficacy by Suppressed Oxygen Inhibition

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ABSTRACT

There are many strategies for improved conversion efficacy such as the reduction of oxygen inhibition effects (OIH). Three-component system using the phosphine to reduce the OIH effects during the free radical polymerization of (meth)acrylate monomers has been reported. Addition, near-infrared (NIR) photopolymerization offers advantages of safer, less light diffusion and scattering, and deeper penetration into the materials. This study presents the detailed kinetics, and modeling the conversion efficacy associated with the experimental results of Bonardi et al. (Macromolecules, 2018, 51, 1314-1324). The dual function of the enhancer additive includes: (i) regenerating the photoinitiator, and (ii) producing extra reactive radical. The temporal profiles of the concentration of each of the 3-component system and the associate conversion efficacy are numerically produced. In this study, several new findings showing unique features of various factors influencing the conversion will be demonstrated. For examples, reverse trends (roles) are found in: (i) the light intensity and enhancer concentration, and (ii) the coupling rate constants of radical-oxygen and radical-monomer. The monomer conversion is an increasing function of enhancer, oxygen concentration, and the light intensity. However, they have significantly different steady state features. The steady-state conversion increases from 10\% without the enhancer (with enhancer concentration $[B]_0 = 0$) to (30\%, 50\%, 80\%) for $[B]_0 = (0.5, 1.0, 2.0)\%$. High conversion also requires a long lifetime of the free radical. Finally, the measured conversion profiles at various conditions reported by Bonardi et al. (Macromolecules, 2018, 51, 1314-1324) are compared and analyzed by our modeling.

INDEX TERMS

Kinetic model, photopolymerization, conversion efficacy, oxygen inhibition, near IR.

I. INTRODUCTION

Free radical photopolymerization consists of two types of photoinitiation (PI), in which type-I is related to the direct coupling of the UV-light initiated radical and the monomers; whereas type-II is related to oxygen-mediated crosslink, or visible-light initiated radicals which coupled to the co-initiator [1], [2]. UV lights (360-400 nm) have been commonly used in most type-I photopolymerization of (meth)acrylate monomers [1]–[3]. However, the UV wavelength suffers the disadvantages of being unsafe to skin and eyes, small penetration depth and larger light scattering in tissues [1]. Camphorquinone (CQ), due to its good visible absorption properties, is the most common type-II PI of (meth)acrylates under visible light [4]–[8]. The first three-component system of (CQ)/amine/ (aryliodonium ylides) was reported by Kirschner et al. [8].

In comparison, near-infrared (NIR) light offers advantages of safer, less light diffusion and scattering, and deeper penetration into the materials [1], [2]. Thus, the curing of a thick and filled material can be potentially enhanced compared to curing with UV or visible light. However, the use of NIR...
photoinitiation systems such as cyanine is often associated with a low reactivity and requires a high light intensity [1]. Phthalocyanines and conjugated macrocycles have been used as commercial pigments and dyes having a high molar absorptivity coefficient in the red and NIR wavelength of 650-810 nm [9], [10]. Efficient polymerization conversions using NIR photoinitiation by cyanine/iodonium salt couples are reported by Strehmel et al [9]. Three-component system with a dye as a photosensitizer absorbing in the NIR range, an iodonium salt (as an initiator), and a phosphine (as a co-initiator) was reported, in which the phosphine is used to reduce oxygen inhibition (OIH) during the free radical polymerization of (meth)acrylate monomers [10], [11].

There are many other strategies to reduce (OIH) including: working in an inert or closed environment, increasing the photoinitiator concentration, increasing the light intensity, or light intensity, use of multiple photoinitiators with different rate of initiation, or addition of oxygen scavengers [12], [13]. Furthermore, functionalized monomers which are insensitive to oxygen, such as the thiol-ene and thiol-acrylate-Michael additive systems were also reported [14], [15]. Additive enhancer-monomer were also proposed to improve the curing (crosslink) efficacy by either reducing the oxygen inhibition effect by stable-monomer, or increase the lifetime of radicals in clinical applications [16], [17]. In addition, dual-wavelength (red and UV) photopolymerization was reported, in which pre-irradiation of red-light was used to pre-reduce the OIH [18].

Recently, Bonardi et al [19] reported the first three-component system for high performance NIR (785 nm) photopolymerization of thick methacrylates, which used (i) a borate dye used as a NIR photosensitizer (PS), (ii) an iodonium salt as a photoinitiator (PI) for the free radical polymerization of the (meth)acrylates, and (iii) a dual-function enhancer (phosphine) to prevent oxygen inhibition, and to regenerate the PS upon irradiation, in which a stable radical is coupled with the enhancer.

This study presents the detailed kinetics, and modeling the conversion efficacy associated with the experimental results of Bonardi et al [19]. The dual function of the enhancer additive includes (i) prevention of OIH, and (ii) regeneration of the PS, which will be explored numerically and analytically in a 3-initiator system. The temporal profiles of the concentration of each of the 3-component and the associate conversion efficacy are numerically produced. In this study, several new findings showing unique features of various factors influencing the conversion will be demonstrated. For example, the reverse trends (roles) are found in: (i) the light intensity and enhancer concentration on the PS concentration; and (ii) the coupling rate constants of radical-oxygen and radical-monomer coupling. Finally, the measured conversion profiles at various conditions reported by Bonardi et al [19] are compared and analyzed by our modeling.

We note that due to the complexity of the kinetics, this article is highly theoretical. Therefore, for those readers without a strong theoretical background may skip the mathematical portion and focus on the kinetics shown by Fig. 1 and section 3.3. Summary of important features which provides all the important issues explored by this article. In addition, readers may read the measured data reported by Bonardi et al [19] which also explained the important features as predicted by our analytic formulas.

II. MATERIALS AND METHODS
A. PHOTOCHEMICAL KINETIC

As shown by Fig. 1, the kinetic scheme of a 3-initiator system, [C], [A] and [B], in the presence of oxygen is proposed. Under the NIR exposure, the initiator dye (C) is excited to its excited-state, or triplet-excited state, given by C∗, which could react with initiator [A] to produce active radical (R) or react with co-initiator [B]; where dye [C] is regenerated in both reactions. The coupling of radical [R] and oxygen [O2] produces a peroxy radical [ROO], which is too stable for the polymerization to proceed. Therefore, an enhancer-initiator [B] is required to create less stable radical [RO] for extra crosslinks of the monomer, [M]. We note that the initiator [B] plays a dual-function of: (i) regeneration of dye [C], and (ii) reducing OIH by generating an extra active radical [RO] for improved conversion. Without the dual-function enhancer [B], OIH reduces the radical [R] and the conversion efficacy, in which an induction time is defined for the delayed rising of the conversion curve [13].

Example of above system was reported by Kirschner et al [8], in a 3-component system of C/B/A, in which [C] = IR-140 borate, [B] = 4-(Diphenylphosphino)benzoic acid (4-dppba), and [A] = iodonium salt Ar2I+PF6−, with initial concentration of [0.1/2.0/3.0] wt%, and mixed in a monomer [M] = methacrylate.

The kinetic equations for our previous single-initiator systems are revised for the 3-initiator system as follows [9]–[12]

\[
\frac{d[C]}{dt} = -b[C] + (k_1[A] + k_2[B] + k_3) C^* \tag{1}
\]
where \( b = 83.6a'wq \), with \( w \) being the NIR light wavelength (in cm) and \( q \) is the excited state \( C^* \) quantum yield, \( a' \) is the mole absorption constant, in \((1/mM/cm^2)\) and light intensity, \( I(z,t) \) in mW/cm^2.

We will use the so-called quasi-steady state assumption [5] described as follows. The life time of radical \( C^* \) and \( [RO] \) are very short (ns to \( \mu \)s time scale) since they either decay or react with the substrate monomer after they are created. However, \([ROO] \) is a rather stable radical and could not be assumed at a steady-state. The steady-state solutions of Eq. (4) to (6) for the radicals of \( C^* \) and \([RO] \) lead to \( C^* = blg[C] \), and \([RO] = k4g'[ROO][B] \), with \( g = k7/k5+k1[A]+k2[B]+k7[M] \), and \( g' = k/(k6+k5)[M], kijlj \). Using these steady-state values, Eq. (1) to (9) reduce to

\[
\begin{align*}
\frac{\partial [C]}{\partial t} &= -B3[M] \quad \text{(10)} \\
\frac{\partial [A]}{\partial t} &= -k1B3[A] \quad \text{(11)} \\
\frac{\partial [B]}{\partial t} &= -k2B3[B] - [RO]/g' \quad \text{(12)} \\
\frac{\partial [ROO]}{\partial t} &= k3[R][O2] - k5[M][RO] \quad \text{(13)} \\
\frac{\partial [R]}{\partial t} &= k1B3[A] - (k'M + k5[O2])[R] - 2kT[R]^2 \quad \text{(14)} \\
\frac{\partial [O2]}{\partial t} &= -k3[R][O2] \quad \text{(15)} \\
\frac{\partial [M]}{\partial t} &= -(k5C^* + k3[RO]+k'[R])[M] \quad \text{(16)}
\end{align*}
\]

where \( B3 = bgl[C] \) and the steady-state radical \([RO] = k4g'[ROO][B] \), or \([RO] = (k3k5)(R[O2])[M] \), if we also use the steady state of \([ROO] \) in Eq. (5). We note that the radical \([R] \) and conversion is a decreasing function of the oxygen initial concentration, as shown by Eq. (14), whereas conversion is improved by enhancer \([B] \) via its dual function of (i) regenerating the dye \([C] \), and (ii) generating extra radical \([RO] \), as shown by the second term of Eq. (16), \( k5[RO] \).

The dynamic light intensity is given by [9], [10]

\[
\frac{\partial I(z,t)}{\partial z} = -A'(z, t)I(z, t) \quad \text{(17)}
\]

\[
A'(z, t) = 2.3[(a'-b')[C](z, t) + b'C_0F' + Q] \quad \text{(18)}
\]

where \( a' \) and \( b' \) are the extinction coefficients of Initiator-C and the photolysis product, respectively; \( Q' \) is the absorption coefficient of the monomer at NIR wavelength. All the reaction rate constants are defined by the associated coupling terms. For examples, in Eq. (4), \( k' \) and \( k'' \) are the coupling of \([R] \) and \([M] \), and \( R \) and oxygen \([O2] \), respectively; and a bimolecular termination rate of \( kT \); \( R \) also couples with initiator \([A] \) and \([B] \) by a rate constant of \( k1 \) and \( k2 \), respectively. Greater detail may be found in Ref. [9], [10]. We note that the dynamic feature of Eq. (17) due to the depletion of \( C(z,t) \) and the spatial dependence of both \( I(z,t) \) and \( C(z,t) \) are critical in optically-thick polymers [10].

The steady-state radical of Eq. (13) is given by

\[
R = \left( \frac{1}{4kT} \right) (-G + \sqrt{G^2 + 8kTBg[C][A]}) \quad \text{(19)}
\]

where \( G = k'[M]+k3[O2] \).

For the radical \([R] \) dominant case with \( 8kTbIC \gg G^2 \), we obtain an approximate radical given by

\[
R = \sqrt{0.5(bg[C][A])/kT} - G/(4kT) \quad \text{(20)}
\]

which is a decreasing function of the oxygen inhibition term \( G \). We note that the conversion is a decreasing function of the oxygen inhibition, whereas conversion is improved by enhancer \([B] \) via the dual function of (i) regeneration of dye \([C] \), and (ii) reducing OIH by generating an extra active radical \([RO] \).

### B. ANALYTICAL FORMULAS FOR EFFICACY

The monomer conversion efficacy for a bimolecular termination process is given by \( CEFF = 1-[M]/[M]_0 = 1-exp(S) \), with \([M]_0 \) being the initial monomer concentration, and the \( S \)-function is given by the time integral of the total rate factor \( R_T \) given by, \( d[M]/dt = -R_T[M] \), in which RT has two components given by Eq. (16).

Solutions of Eq. (10) to (18) are available by the approximated analytic formulas for \( I(z,t) \) as follow [2], [4]

\[
I(z,t) = I_0 \exp[-A'z] \\
A'(z,t) = 2.3(a'C_0 + Q) - A_1t \\
A_1 = 2.3(a'\cdot b')C_00Hz
\]

where \( A_1 = 2.3(a'\cdot b')C_00Hz \). We note that the \( -A_1t \) term represents the decrease of \( A' \), or increase of light intensity due to PS depletion, which is important for optically-thick polymers.

Using Eq. (21) and for \( (k3k7+ k1[A]+k27[B])<<[M] \), \( g=1/[M] \), solution of Eq. (10) gives us

\[
C(z, t) = C_0 \exp[-B'(t)] \\
B'(t) = b \int I(z, t) [1 - H(t)] dt
\]

where \( H(t) = (k3k7+k1[A]+k27[B])/[M] \). We note that \( C(z,t) \) has a longer lifetime or reduced decaying rate due to the H-factor proportional to \( k1[A]+k27[B] \), which could enhance the efficacy. As shown by Eq. (18), larger \( C(z,t) \) enhanced by \( H \)-factor will improve the efficacy by an increased radical \( R \).
When $H=0$, analytic solutions of $C(z,t)$ and efficacy are available as follows

$$C(z,t) = C_0 \exp\left[ -B't \right]$$

where $B' = b_{10}\exp(-A'\cdot z)-0.5A_{1t}$, with $A_0 = 0.5 \times 2.3 \, (a'+b')^{+}+2.3Q$, $A'$ being the averaged absorption given by $A' = 0.5 \times 2.3(a'+b')^{+}+2.3Q$. Given above $C$, we may find the radical of Eq. (20) and then the conversion efficacy $C_{\text{EFF}} = 1-\exp(-S)$, with $S(z,t)$ given by, for $g' \ll k'$, and ignored $A_1$,

$$S = KG(z,t)\sqrt{0.5bXI_0C_0} \quad (25)$$

$$G'(z,t) = [1-\exp(-B''t)]/B'' \quad (27)$$

where $K=k'/k''$, $B''=0.5(B'-0.5A_{1t})$, $X=\exp(-A_{2}z)$. We note that when $H$-factor is included, $B''$ is reduced with higher $S$ and conversion.

For analytic solution of Eq. (23), we could solve for the approximated solution of Eq. (11) and (12) for $[A]$ and $[B]$ as follows: $[A]=[A_0]-bICG'$, and $[B]=[B_0]-bICG'$. Therefore, the time integral of $H(t)$ proportional to $([A_0]+[B_0])t$ less than the time integral of $G'(t)$. Eq. (25) shows $B'(t)$ is reduced by a factor proportional to $([A_0]+[B_0])t$, which enhances the conversion, comparing to when $[A]-[B]=0$. Numerical solutions of Eq. (15) will be shown later, without the above described assumptions.

For the case when $k_{5}[RO]$ is dominant in Eq. (16), given the steady-state solution of Eq. (5) and (6) leads to $[RO]=(k_3/k_5)(R[O_2]/[M])$, which gives the solution of Eq. (16)

$$M(t) = M_0 - k_3 \int_0^t [R][O_2]dt \quad (28)$$

Therefore, by the definition of efficacy $C_{\text{EFF}} = 1-M/M_0$, we obtain

$$C_{\text{EFF}} = \left( \frac{k_3}{M_0} \right) \int_0^t [R][O_2]dt \quad (29)$$

where radical $[R]$ is proportional to $bICg$, but is a decreasing function of oxygen, as shown by Eq. (20). We note that $g= \frac{k_3}{k_5+k_1[A]+k_2[B]+k_7[M]}$, and $g'=1/(k_6+k_5'[M])$, are decreasing function of the rate constant $k_5$ and $k_5'$, and inverse proportional to the life time of $C^*$ and $[RO]$, respectively. We note that there is no analytic solution for Eq. (29), which could be solved only numerically $[R]$ and $[O_2]$ to obtain the time integral. Numerical results will be shown later.

III. RESULTS AND DISCUSSION

If We note that the radical $[R]$ and conversion is a decreasing function of the oxygen initial concentration, as shown by Eq. (14), whereas conversion is improved by enhancer $[B]$ due to its dual function of: (i) regenerate the dye $[A]$, and (ii) generate extra radical $[RO]$, as shown by the second term of Eq. (16), $k_5[RO]$. The influencing factors of conversion to be explored numerically include: the initial concentrations $[A_{0}], [B_{0}], C_0$ and oxygen $[O_{20}]$, the coupling constant $B_3 = gbIC$, the $g$-functions $g$ and $g'$, and the rate constants, $k_{ij}$, specially $k_5$, the coupling between $[RO]$ and $[M]$. We note the coupling constant $b$, a product of $b$ and light intensity ($I$), will be considered as one parameter which also represents the light intensity for a given absorption constant ($b$).

A. DYNAMIC PROFILES

Figure 2 shows the role of the enhancer initial concentration $[B_{0}]$ (shown by Figure (A), and the coupling constant $b_{10}$ (shown by Figure (B), for fixed $[A_{0}], [C_{0}]$ and $[O_{20}]$. These profiles show that the conversion is an increasing function of $[B_{0}]$ and $b_{10}$. However, unlike Figure (A), Figure (B) shows the same steady-state conversion. This feature could be realized by the radical $[RO]$ profiles shown in Figure 3, in which Figure 3(A) shows increasing areas covered by curves 1,2,3, and 4. In contrast, Figure 3(B) shows the same the area covered by all 4 curves. Our new finding could be further explored by Eq. (16) that when the second term, $k_{5}[RO]$, is dominant, the efficacy is mainly governed by the time integral or the area covered by the $[RO]$ profile shown in Figure 3. This also demonstrates the consistent trends of Figure (A) and (B) in Figure 2 and Figure 3.
and oxygen [O\textsubscript{2}], in which [R] and [O\textsubscript{2}] are, respectively, an increasing and decreasing function of time. Therefore, the combined effect leads to the optimal (or peak) of the temporal profile of [RO]. Furthermore, a larger co-initiator concentration ([B]\textsubscript{0}) leads to a larger radical [RO] as shown in Figure 3 (A). In contrast, a higher light intensity leads to a faster oxygen depletion and thus a faster drop of [RO] profile as shown in Figure 3 (B).

Figure 4 and 5 show the concentration profiles of initiator C(t), and oxygen [O\textsubscript{2}] associate to Figure 2(A) and 2(B), respectively. We note that C(t) has a higher value in the presence of enhancer ([B]) due to the regeneration of C, shown by Figure 4 having various [B]\textsubscript{0}. In contrast, a reversed trend is shown by Figure 5 having various coupling constant of b' = bI\textsubscript{0}, in which a larger b' leads to a stronger depletion and lower value of C(t).

![Figure 4](image)
**Figure 4.** The concentration profiles of initiator C(t), and oxygen [O\textsubscript{2}] associate to Figure 2(a).

![Figure 5](image)
**Figure 5.** Same as Figure 4, but associate to Figure 2(B).

Figure 6 shows the role of oxygen—that a higher initial oxygen concentration achieves a higher efficacy, as also predicted Eq. (16) which has three components given by B\textsubscript{3} = gbIC, k\textsubscript{5}[RO] and k'R. The steady-state solution of Eq. (5) and (6) leads to k\textsubscript{5}[RO] = k\textsubscript{3}[R][O\textsubscript{2}]/[M]), which is an increasing function of oxygen. In the absence of oxygen, radical [RO]=0, the efficacy is given by gbIC and k'R, as shown by curve-1 of Figure 6(B). In contrast, for the k'R dominant case, conversion is reduced by OIH, as shown by Eq. (20), in which bimolecular termination leads to a reverse-trend of light intensity, i.e., a lower intensity leads to a higher steady state conversion.

![Figure 6](image)
**Figure 6.** The oxygen profile (a), and conversion profile (b), for various initial oxygen concentration of [O\textsubscript{2}]\textsubscript{0} = (0, 0.25, 0.5, 1.5) mg/L, with [A]\textsubscript{0} = 3.0%, [B]\textsubscript{0} = 2.0%, [C]\textsubscript{0} = 0.1%, b\textsubscript{I} = 0.6 (1/s/5).

Figure 7(A) shows that efficacy is an increasing function of k\textsubscript{3}, (a reaction rate between [R] and [O\textsubscript{2}]), but a decreasing function of the rate constant k\textsubscript{5}. This reverse-trend could be realized by B\textsubscript{3} = gbIC, which is a decreasing function of the rate constant k\textsubscript{5}. We note that g = k\textsubscript{7}/(k\textsubscript{5} + k\textsubscript{1}[A] + k\textsubscript{2}[B] + k\textsubscript{7}[M]), and g' = 1/(k\textsubscript{5} + k\textsubscript{5}' [M]), are decreasing function of the rate constant k\textsubscript{5} and k\textsubscript{5}', which are inverse proportional to the life time of C* and [RO], respectively. Therefore, shorter radical life time (or larger k\textsubscript{5}) of C* or [RO] leads to lower conversion. To achieve a higher conversion a longer lifetime (or smaller k\textsubscript{5}) is requires.

![Figure 7](image)
**Figure 7.** Conversion profiles for various rate constants:
(a) k\textsubscript{3} = (1, 2, 4, 8) (1/s); and (b) k\textsubscript{5} = (1, 2, 4, 8) (1/s), with other fixed parameters same as that of Figure 2.

B. ANALYSIS OF MEASURED DATA
The measured data shown by Figures 4, 6 and 10 of Bonardi et al [19] could be compared to our modeled results as follows. Figure 8 shows that higher coupling constant b' = bI\textsubscript{0} leads to higher efficacy, which is also an increasing function of light intensity, as shown by Figures 4, 6 and 8 of Bonardi et al [19]. Furthermore, the photolysis (% decomposition of the peak at 800 nm) upon laser diode at 785 nm, shown by Figure 10 of Bonardi et al [19] could be compared with our Figure 4(A) for the initiator concentration C(t), in which a higher enhancer concentration [B] leads to a higher C(t), or less depletion due to the regeneration of C(t) by the enhancer [B]. We note that the photolysis or the
Relative peak spectrum height at 800 nm, D(t) reported by Bonardi et al. [19], is related to C(t) by D(t) = C(t)/C_0.

Numerical results shown by Figs. 2 to 10, and our analytic formulas provide the following important features:

(i) The radical [R] and conversion are reduced by the oxygen inhibition, as shown by Eq. (14), whereas conversion is improved by enhancer [B] via dual function of (i) regeneration of the dye [C], and (ii) producing extra radical [RO]. The conversion is an increasing function of enhancer and oxygen concentration, and the coupling constant, b' = bI_0. However, they have significantly different steady state feature. High conversion also requires a long lifetime (or smaller k_s) of the free radical [RO]. The steady-state conversion increases from 10% without the enhancer (with oxygen inhibition, as shown by Eq. (14)), whereas conversion is an increasing function of enhancer and oxygen concentration, and the coupling constant, b' = bI_0, and a decreasing function of k_s, which is inverse proportional to the lifetime of [RO], i.e., high conversion requires a long lifetime (or smaller k_s).

We suggest that readers should read the measured data reported by Bonardi et al [19], which also explained the important features as predicted by our analytic formulas and our numerical results. For a more comprehensive modeling, readers may refer to Ref. [20]. This article explores the kinetics of a single-wavelength system. We also suggest readers to read our other articles which further explored 2-wavelength and 3-wavelength polymerizations [23], [24] for the applications in 3D bioprinting.

IV. CONCLUSION

We have demonstrated that efficacy of NIR photopolymerization could be enhanced by an enhancer [B] via dual function of (i) regeneration of the dye [C], and (ii) producing extra radical [RO]. The conversion is an increasing function of enhancer and oxygen concentration, and the coupling constant, b' = bI_0. However, they have significantly different steady state feature. High conversion also requires a long lifetime (or smaller k_s) of the free radical [RO]. The steady-state conversion increases from 10% without the enhancer (with oxygen inhibition, as shown by Eq. (14)), whereas conversion is an increasing function of enhancer concentration [B]_0, and the coupling constant, b' = bI_0, as shown by Eq. (16), k_3[RO].

We have demonstrated that efficacy of NIR photopolymerization could be enhanced by an enhancer [B] via dual function of (i) regeneration of the dye [C], and (ii) producing extra radical [RO]. The conversion is an increasing function of enhancer and oxygen concentration, and the coupling constant, b' = bI_0. However, they have significantly different steady state feature. High conversion also requires a long lifetime (or smaller k_s) of the free radical [RO]. The steady-state conversion increases from 10% without the enhancer (with oxygen inhibition, as shown by Eq. (14)), whereas conversion is an increasing function of enhancer concentration [B]_0, and the coupling constant, b' = bI_0, as shown by Eq. (16), k_3[RO].

CONFLICTS OF INTEREST

Jui-Teng Lin is the CEO of Photon Vision Corp., Taipei, Taiwan. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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