Influence of number of catalyst sites in 1,3-butadiene solution polymerization catalyzed by titanium tetrachloride

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Funding information
Conselho Nacional de Desenvolvimento Científico e Tecnológico; Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro

Abstract
The synthetic rubber industry is of great importance and it is present in the daily life of world society. Butadiene rubber or polybutadiene is one of the most used polymers in this field, mainly in tire production. Therefore, the control of operational conditions and final properties of the polymer formed are important points to be studied as they are a challenge for the industry. Thus, the present work focus in simulate the batch polymerization of polybutadiene using the Aspen Plus software, where 1,3-butadiene, titanium tetrachloride, triethylaluminium, and hexane were used as monomer, catalyst, cocatalyst and solvent, respectively. Four cases were simulated changing the number of active catalyst sites in order to predict and compare the final properties of polybutadiene resins including the average molar masses, the molar mass distribution and the evolution of operation conditions that are used at plant to monitor the course of the reaction like the reaction temperature and pressure. The simulations show that three and four active catalyst sites are capable to synthesize polymers with similar properties than commercial and bench-scale polybutadienes.

KEYWORDS
Aspen Plus, molecular mass distribution, polybutadiene, simulation

1 | INTRODUCTION

Rubber is a kind of polymer that can be natural or artificial and it is an important material used in the tire industry, footwear, automotive accessories, health related products, among others. Natural rubber is obtained from latex, which is produced in many tropical plant species. Almost all the world’s natural rubber production comes from the rubber tree (Hevea brasiliensis) latex extraction, although many tropical plant species produce this material.1

Natural rubber has some properties that make their use difficult. For example, in cold temperatures, it becomes hard and brittle, while in higher temperatures it becomes soft and sticky. Due to this fact, in 1839, Charles Goodyear started to research the process called vulcanization. In this process, sulfur was added to the polymer causing its double bonds to break and form sulfur bridges that bind the side chains, decreasing hysteresis, reducing permanent deformation, and increasing elasticity.2
From then on, studies began to be carried out on the addition polymerization reactions of dienic compounds, producing many types of synthetic rubbers. Depending on the type of monomer used to make the polymer, rubbers with distinct properties can be achieved.

The object of this study is polybutadiene rubber, one of the most used elastomers on the rubber industry. It is also called simply butadiene rubber (BR), it is predominantly based on cis-1,4 polybutadiene and its synthesis require a catalyst usually based on a transition metal, specially the lanthanides' metals. Among the metals most used as catalysts are neodymium, cobalt, titanium, and nickel and, in spite their differences, they all synthesize polybutadienes with 1,4-cis content above 90%.

The structure of the polymer obtained from 1,3-butadiene indicates the addition occurs preferably in the 1,4 positions. Notably, the carbon chain still has a double bond. Although the isomer trans is the most stable, when catalysts based on neodymium or titanium are used, the polymer chain tends to be formed by cis isomers.

The polymer has important characteristics that directly influence the properties of the final product such as melting temperature, crystallinity, malleability, and flexibility. One of these properties is the number average molar mass ($M_n$) and mass average molar mass ($M_w$). The first one is calculated by adding the molar masses of all chains generated throughout the process and dividing it by the total number of chains. On the other hand, $M_w$ is calculated taken into account the molar mass of each polymeric chain fraction.

\[
M_n = \frac{\sum n_i \cdot M_i}{\sum n_i},
\]

\[M_w = \frac{\sum n_i \cdot M_i^2}{\sum n_i \cdot M_i},\]

$M_i$ — molar mass of the chain

$n_i$ — number of molecules with mass $M_i$

Another important property is the dispersity that indicates the relationship between $M_n$ and $M_w$. The more varied the sizes of the molecules, the greater is the dispersity value (which is always greater than 1). On the other hand, when chain sizes are close, the polydispersity is approximately 1.

\[
PDI = \frac{M_w}{M_n}.\]

Polybutadiene fills about 25% of the world rubber market. It can be obtained in different ways, which differ in terms of molecular microstructure, average molar masses, molar mass distributions (MMD), degree of branching, types of branching, and functionalization of terminal groups. It can be obtained through different types of catalysts, and free radical, cationic, anionic or coordination initiators can be used.

The high-cis polybutadiene is catalytically produced by Ziegler-Natta (ZN) catalysts. Among the ZN, cobalt, nickel, titanium, and neodymium-based catalysts are the most employed.

BR is used in four major areas: tire manufacturing (70%); impact alteration of thermoplastics (25%) such as high impact polystyrene and acrylonitrile butadiene styrene terpolymer, more commonly known as ABS; and everyday products such as shoe soles and golf balls (5%).

As there is a high demand for improvements of the mechanical properties of rubbers used by the tire industry, the production of high-cis polybutadiene has been the subject of several scientific studies in recent years.

ProB et al. presented a mathematical model for 1,3-butadiene polymerizations with a neodymium-based catalyst and were able to predict the MMD of the final product, the evolution of 1,3-butadiene concentrations and the dependence of the reaction rate constant on the Cl/Nd molar ratio. The authors showed that distinct catalytic systems presented distinct kinetic constants and produced rubbers with distinct properties.

Ling et al. proposed a Monte Carlo procedure to simulate the gas phase polymerization of 1,3-butadiene and were able to predict the MMD of the obtained products.

Aminova et al. developed a mathematical model to describe 1,3-butadiene polymerizations using a cobalt-based catalyst. The author’s proposed model was able to simulate $M_n$ and $M_w$, branching factors and sedimentation-average degrees of polymerization. It was observed the occurrence of branching reactions, chain transfer to polymer, and chain crosslinking. In another work, Aminova et al. improved the same model in order to describe a continuous process and used the model to simulate the average molecular weights of the obtained products.
Manuiko et al.\textsuperscript{12} proposed a model for 1,3-butadiene solution polymerizations that considers the presence of two types of active sites in the system and the presence of hexachloro-p-xylene as a chlorinating agent. Particularly, their model was able to calculate average molecular weights and branching frequencies.

Vasconcelos et al.\textsuperscript{13} developed a mathematical model for the polymerization of 1,3-butadiene using neodymium versatate as a catalyst. Their model was able to predict final properties of the polybutadiene polymer as average molar masses and cis-content, and also the evolution of operation conditions that was used at plant site to monitor the course of the reaction such as temperature and pressure.

Although the model of Vasconcelos et al.\textsuperscript{13} predicted the average data, microstructure, temperature, and pressure profiles very well, the PDI values are well above 2, suggesting the existence of more than one active catalyst site. Possibly, their model would not perform optimally to represent the MMD. Ferreira et al.\textsuperscript{6} developed a model considering four active catalyst sites for the butadiene’s polymerization. Although the model performed well to represent the MMD, it was a very complex model that had to be simplified in order to be solved.

As related by Ferreira et al.,\textsuperscript{6} the existence of more than one active catalyst site, with different kinetic constants each one, directly affect the polymer final properties. Therefore, it is important to consider the presence of more than one active catalyst site in coordination polymerizations that use ZN catalyst.

Many studies reported the use of titanium tetrachloride (TiCl\textsubscript{4}) for 1,3-butadiene solution polymerizations such as Marques and Coutinho, Gaylord et al., and Zohuri et al.\textsuperscript{14-16} For this catalyst, it is well known that the presence of multiple active catalyst sites is directly linked to the titanium valence number that can be +2, +3, and +4. Pokasermsong and Praserthdam\textsuperscript{17} made an experimental study in order to widely investigate these transition metal oxidations through electron spin resonance spectroscopy and discovered that Ti\textsuperscript{3+} species are considerably active to run the polymerization. The appearance of Ti\textsuperscript{3+} species is associated with Al/Ti ratios showing that an increase in this ratio causes a decrease in the catalyst activity. Therefore, the organoaluminum cocatalyst plays an important role in the active catalyst site formation by alkylation and reduction of the titanium species.\textsuperscript{18}

To the best of our knowledge, given the described scenario, there are not many theoretical studies that investigate the number of types of active sites in the polymerization and their influence on the polymer MMD, as well as temperature and pressure profiles during the process. Thus, the present work investigates the influence of the number of titanium tetrachloride active catalyst sites on the 1,3-butadiene solution polymerization using Aspen Plus 10 software.

2 | MATERIALS AND METHODS

The selected methodology for simulating polybutadiene polymerization was based on that described in Aspen Plus Chemical Engineering Applications for the process of forming HDPE.\textsuperscript{5} First, the Aspen template chosen to run the simulation was “Polymers with Met - C_bar_hr Units” and then the physical property method polymer nonrandom two-liquid property method was selected. The polymerization process was simulated using a batch reactor and a flash column as shown in Figure 1.

Since the objective of the current work was not focused on varying the process conditions, but to verify the influence of the number of active catalyst sites on the final polymer properties and reactor temperature and pressure, we kept constant all operational conditions. Gaioto et al.\textsuperscript{19} reported the temperature of 70°C was the one responsible to obtain higher yield in the range of 60–80°C. For this reason, we chose 70°C as the initial reaction temperature.

\textbf{FIGURE 1} Main Flowsheet of the polybutadiene polymerization process
TABLE 1 Components added in the simulation

| Component                | Molecular formula | Function in process | Molar fraction in feeding |
|--------------------------|-------------------|---------------------|--------------------------|
| N-hexane                 | C₆H₁₄             | Reaction solvent    | 8.31 × 10⁻¹              |
| 1,3-butadiene            | C₄H₆              | Monomer             | 1.30 × 10⁻¹              |
| Polybutadiene            | (C₄H₆)ₙ           | Polymer             | –                        |
| Butadiene R-1           | C₄H₆·R            | Segment             | –                        |
| Titanium tetrachloride   | TiCl₄             | Catalyst            | 4.85 × 10⁻⁵              |
| Triethylaluminium        | (C₂H₅)₃Al         | Cocatalyst          | 8.92 × 10⁻⁵              |
| Nitrogen gas             | N₂                | Inert gas to pressurize | 3.86 × 10⁻²               |

*The component Butadiene-R1 corresponds to a living polymer with size i.*

The supply stream (FEED) of the reactor for all cases had a temperature equal of 70°C and pressure of 2.66 bar. The FEED molar flow was 3.88 mol h⁻¹ and the molar fraction of each component is shown in Table 1 with the reaction components considered in the simulation. The molar fraction of each component was calculated based on the mass of butadiene, volume of n-hexane and catalyst and cocatalyst molar concentrations reported by Vasconcelos et al. In order to pressurize the system to achieve the pressure reported by Vasconcelos et al., we added to the reactor 0.15 mol of nitrogen gas. The reactor used was a batch reactor with volume equal to 10 L and constant thermal fluid temperature operating at 70°C with heat transfer coefficient of 2.19 × 10⁻³ kJ (s m² K)⁻¹. The chosen reactor operating time was 2 h.

The flash tower following the batch reactor is responsible to separate the polymer fraction to the vapor fraction as seen in Figure 1.

As seen in the literature, it is known that polybutadiene has essentially linear structure and high cis-content (greater than 90%) when the used catalyst is based on titanium. Therefore, it was decided to disregard the trans monomer during the simulation. The kinetic mechanism considers the following steps described in Equations (4)–(6).

- **Initiation step**

  \[ M + \text{Cat}^* \rightarrow P_1^*(\text{cis}), k_i \quad (4) \]

- **Propagation step**

  \[ P_i^* + M \rightarrow P_{i+1}^*, k_p \quad (5) \]

- **Transfer to monomer Step**

  \[ P_i^* + M \rightarrow D_i + P_n^*, k_{tm} \quad (6) \]

where, \( k_i \) is initiation kinetic rate constant; \( k_p \) is the propagation kinetic rate constant; \( k_{tm} \) is the transfer to monomer kinetic rate constant; \( M \) is butadiene; \( \text{Cat}^* \) represents the active catalyst site; \( P_1^* \) is a living polymer chain with size 1; \( P_i^* \) is a living polymer chain with size \( i \); and \( D_i \) is a dead polymer chain with size \( i \).

Although in the work of Vasconcelos et al. the butadiene polymerization was synthesized with a neodymium-based catalyst with one active catalyst site, we assumed the same values of kinetic rate constants (\( k_i, k_p, k_{tm} \)) and activation energies for propagation and transfer to monomer reactions to represent the same kinetic mechanism but using a TiCl₄ catalyst. This is a model assumption adopted since, to the best of our knowledge, there are no works of kinetic model with TiCl₄ for butadiene polymerization. This first model (with a unique catalyst site) is latter modified generating other case studies and new constants were estimated.
Table 2: Kinetic rate constants used for simulations

| Case study | Number of sites | \(k_i\) (s\(^{-1}\)) | \(k_{p0}\) (L mol\(^{-1}\) s\(^{-1}\)) | \(k_0\) (L mol\(^{-1}\) s\(^{-1}\)) | \(k_{tm0}\) (L mol\(^{-1}\) s\(^{-1}\)) |
|------------|----------------|----------------|----------------|----------------|----------------|
| I          | 1              | 1–1.74 × 10\(^{-1}\) | 1–2.29 × 10\(^{15}\) | 1–89.2 | 1–5.5 × 10\(^{13}\) |
|            |                | 2–2.61 × 10\(^{-2}\) | 2–1.02 × 10\(^{16}\) | 2–397.2 | 2–5.5 × 10\(^{13}\) |
| III        | 3              | 1–1.74 × 10\(^{-1}\) | 1–2.29 × 10\(^{15}\) | 1–89.2 | 1–5.5 × 10\(^{13}\) |
|            |                | 2–2.61 × 10\(^{-2}\) | 2–1.02 × 10\(^{16}\) | 2–397.2 | 2–5.5 × 10\(^{13}\) |
|            |                | 3–1.74 × 10\(^{-1}\) | 3–6.84 × 10\(^{15}\) | 3–266.3 | 3–5.5 × 10\(^{13}\) |
| IV         | 4              | 1–1.74 × 10\(^{-1}\) | 1–2.29 × 10\(^{15}\) | 1–89.2 | 1–5.5 × 10\(^{13}\) |
|            |                | 2–2.61 × 10\(^{-1}\) | 2–2.75 × 10\(^{15}\) | 2–107.1 | 2–5.5 × 10\(^{13}\) |
|            |                | 3–1.74 × 10\(^{-1}\) | 3–8.01 × 10\(^{15}\) | 3–311.9 | 3–5.5 × 10\(^{13}\) |
|            |                | 4–5.79 × 10\(^{-3}\) | 4–6.41 × 10\(^{15}\) | 4–249.6 | 4–5.5 × 10\(^{13}\) |

Note: Values of energy of activation were 88.09 kJ mol\(^{-1}\) for all propagation steps and 96.405 kJ mol\(^{-1}\) for all transfer to monomer steps. It is important to mention that \(k_i\) does not vary with temperature, while \(k_{p0}\) and \(k_{tm0}\) are the preexponential factor of the kinetic parameters \(k_p\) and \(k_{tm}\) that follow the Arrhenius equation.

As aforementioned, it is known the number of active catalyst sites affects the final polymer properties. Thus, four case studies were chosen to verify how these catalyst sites affect the temperature and pressure reactor profiles, average molar masses and MMD. The first case study considers just one catalyst site with the parameters equivalent to the ones reported by Vasconcelos et al. From the second to the fourth case study it was considered an even distribution for the active catalyst sites (e.g., for 2 sites → 0.5 fraction of site 1 and 0.5 fraction of site 2). An exhaustive search for the parameters was done for case studies II, III, and IV to achieve PDI around 3, 4, and 5, respectively. These PDI values are within the PDI range reported for commercial and bench-scale polybutadienes and correspond to number and mass average molar masses reported in literature.

3 | RESULTS AND DISCUSSION

Four different scenarios were simulated in Aspen Plus and the differences between each other was in the number of types of active sites and the kinetic rate constants of each site. In case studies II, III, and IV, the MMDs graphs show the curves of each catalyst site and their convolution that represents the polymer.

For case study I, there is only a unique curve because there is just one catalyst site. Thus, the MMD of the catalyst site matches with the polymer MMD. The data was treated and normalized to be presented in this work.

It can be seen in Figure 2 the MMD considering only a single catalyst site did not present bimodality, as expected, since the presence of only one active center generates only a group of polymers following reactions with the same kinetic constants. In addition, a polydispersity index of 2.02 is observed, something very similar to a free-radical polymerization process following the Flory distribution, which is expected for a catalyst with only one active center.

The average molar masses are of the order of 3.61 × 10\(^4\) and 7.31 × 10\(^4\) g mol\(^{-1}\) for \(M_n\) and \(M_w\), respectively, which are considered low average molar masses for a solution polymerization of 1,3-butadiene. In Figure 3, the resultant MMD for case study II can be seen.

Comparing Figures 2 and 3, it is noted that Figure 3 presents a bimodality, while Figure 2 does not. This is expected, since the presence of two active centers with different kinetic constants generates polymer chains with different growth rates, which leads to the widening of the distribution and the appearance of bimodality. This bimodality can be seen in the polydispersity index, which jumped from 2 to 3.25 due to the presence of another active center. The preparation of the catalyst strongly influences the presence of the active centers, since the choice of reagents, the preparation time, the preparation method, the reaction temperature, the storage temperature, and the order of the reagents determine the formation of the active centers of the catalyst.

An increase in the average molar mass for case study II was expected as there is a change in the reaction kinetics based on a change in the number of active catalyst sites with different values of propagation kinetic rate constants. As the \(k_{tm}\)
values were kept constants, the modification in the average properties were primarily due to the increase in the number of active catalyst sites. The change in polydispersity value is also expected as it is a function of the average molar masses. Therefore, a change in the values of $M_n$ and $M_w$ also results in changes in PDI.

Thus, considering the experimental conditions were kept constant for all case studies, when we run the simulation of the case study II, the second catalyst site has higher $k_p$ than the first one, so active site 2 propagates at higher rate producing polymers with longer chains. The average molar masses are then increased when compared with the ones when just one catalyst site is active, since their calculation takes into account the size of each chain.

Although the average molar masses rise, this increase is still not very significant in the general context of polybutadiene, because of that, a further simulation was carried out now with three active sites, which is shown in Figure 4.

Now comparing Figures 3 and 4, it can be seen that bimodality remains present regardless of having more active centers. One more time, there is an expressive increase in the polydispersity index to 4.13 indicating that the increase
**Figure 5** Molar mass distribution of polybutadiene considering four active catalyst sites

| Number of sites | $M_n \times 10^4$ (g mol$^{-1}$) | $M_w \times 10^4$ (g mol$^{-1}$) | PDI |
|-----------------|----------------------------------|----------------------------------|-----|
| 1               | 3.61                             | 7.31                             | 2.02|
| 2               | 5.08                             | 16.48                            | 3.25|
| 3               | 11.88                            | 49.07                            | 4.13|
| 4               | 14.06                            | 73.72                            | 5.24|

The number of active centers is directly linked to the widening of the MMD. Regarding the average molar masses, $M_n$ and $M_w$ increased significantly compared with the simulations with one and two active centers, where the average molar masses are in the order of $10^5$ g mol$^{-1}$. Finally, for comparison purposes, the simulation with four active centers is shown in Figure 5.

Comparing Figure 5 with the others, it can be observed that the polymer MMD is significantly wider than the others, that is, the polydispersity index presented by the simulation with four active sites is the highest among the simulations and the closest to the ones found in the literature.$^{13,24}$ The polymer MMD still presents bimodality although all four active catalyst site MMD are unimodal and the average molar masses are even greater than the ones obtained in the previous case studies.

It can be seen in case study I only one unimodal curve, whereas for all other cases the bimodality appeared since each active catalyst site propagated at a certain rate, generating a unimodal MMD for each catalyst site which resulted in a polymer bimodal MMD.

All the average molar masses and polydispersity indexes for all the four case studies are presented in Table 3.

In Figure 6, it can be seen the PDI and $M_w$ of the case studies and some data from literature, where CS I, CS II, CS III, and CS IV corresponds, respectively, to the case studies values I, II, III, and IV obtained in that work, CM and 98-sb corresponds to values of commercial polybutadienes and PB I and PB II corresponds to values obtained in Pires et al., Gaioto, and Brandão et al.$^{7,20,21}$

It can be seen case studies III and IV present PDI and $M_w$ values that resemble with polymers obtained and characterized in other works and with commercial polybutadienes. Mass average molar masses from CM and 98-sb are very similar to the results from case study III, however, only PDI CM is similar to CS III, while PDI 98-sb is close to CS II, indicating commercial is very likely to have during the polymerization three active catalyst centers and 98-sb, something between two and three active catalyst centers. On the other hand, comparing other works from literature, we can see PB II is very close to case study IV for both $M_w$ and PDI values, while PB I is between case studies III and IV. By this analysis, it can be noted there is not a unique value of number of active catalyst sites for butadiene polymerization, highlighting the understanding of this subject is very significant. The operational conditions such as type of catalyst, solvent, temperature, ratio catalyst/cocatalyst have an important influence on the formation and the number of active catalyst sites, therefore it will define the final properties of the manufactured product. Beyond that, the operational conditions also affect the polymerization and consequently the final polymer properties (average molar masses, microstructure, MMD).

The graph in Figure 7 was generated in order to superimpose the polymer MMD curves generated in all cases. As can be seen, the increase of the number of active catalyst sites shifts the curves to the region of higher molar masses. Besides that, it can be noted the difference between the width of each curve, indicating the variation among PDI of each case. As we increase the number of active catalyst sites, the MMD height decreases while the distribution widens.
During the 1,3-butadiene solution polymerization, it is also known that an increase in temperature is expected because polymerization reactions are, for the most part, exothermic reactions that release energy to the system causing an increase in temperature. As we are working with a batch reactor of constant system volume, an increase in temperature directly leads to an increase in pressure. All propagation and transfer to monomer reaction rate constants follow the Arrhenius equation, therefore, an increase in temperature causes an increase in these kinetic parameters and, considering the \( k_{im} \) was kept the same for all sites at all case studies, the increase in temperature then directly causes an increase in the average molar masses. This scenario was exactly what happened in the current work, as shown in the Supplementary Material.

The pressure was basically not affected by the increase of the number of active catalyst sites, since the catalyst weight was kept constant for all case studies, so the reaction conversion was also the same. Knowing the conversion is directly affected by the butadiene consumption, a decrease in the concentration of butadiene in the medium results in a pressure decrease. The pressure profiles for all cases were practically overlapping each other as shown in the Supplementary Material. The pressure peak at the first 10 min of polymerization is due to the temperature increases caused by the start of the initiation and propagation reactions, then both temperature and pressure decreases due to the reduction of monomer available that implies on the reduction of the frequency of propagation and chain transfer to monomer reactions, releasing less energy than before.

The pressure profiles obtained were considered appropriate, because they coincide with the profiles obtained by Vasconcelos et al. for both the data predicted by the model and the experimental data.\(^\text{13}\)

## 4 Conclusion

The present study aimed to evaluate the influence of the number of active catalyst sites in MMD of polybutadiene. 1,3-butadiene polymerizations were performed successfully in Aspen Plus 10 considering one, two, three, and four active catalyst sites. It was possible to reproduce the production of polybutadiene in a commercial simulator with a very good accuracy comparing with commercial polymers without the need of a complex model.
It was concluded that temperature and pressure profiles are practically not changed with a variation in the number of active catalyst sites. Such profiles show an increase until reaching a peak and then stabilize, showing similarity with those already reported in the literature.

Comparing values of $M_n$, $M_w$, and PDI it can be confirmed they are directly related with the growth of the number of active catalyst sites. Values of $M_n$ range from $3.6 \times 10^4$ to $1.4 \times 10^5$, $M_w$ range from $7.3 \times 10^4$ to $7.4 \times 10^5$ and PDI range from 2.02 to 5.24. Besides that, the polymer MMDs generated show the dispersity increases with the increase of the number of active catalyst sites and the distributions dislocated in the region of higher molar masses. Although the commercial polybutadienes presented similarities with case study III (three sites) and other works from literature with case study IV (four sites), we concluded there is not an ideal number of active catalyst site, however, the knowledge of this information is very important to predict the final properties of the rubber, since the number of active catalyst sites widely influences on the average molar masses and the MMDs.

ACKNOWLEDGMENTS
The authors thank CNPq (Conselho Nacional de Pesquisa e Desenvolvimento Científico e Tecnológico) and FAPERJ (Fundação Carlos Chagas Filho de Apoio à Pesquisa do Estado do Rio de Janeiro) for providing financial support and scholarships.

PEER REVIEW INFORMATION
 ENGINEERING REPORTS thanks Alex Ardagh and other anonymous reviewers for their contribution to the peer review of this work.

PEER REVIEW
The peer review history for this article is available at https://publons.com/publon/10.1002/eng2.12333.

CONFLICT OF INTEREST
Authors have no conflict of interest relevant to this article.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section at the end of this article.