Development of a Novel Terpolymer as a Green and Efficient Decalciﬁng Agent for Crude Petroleum

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ABSTRACT: A novel environmental decalciﬁng agent was prepared with allylpolyethoxy amino carboxylate (APEAA), hydroxyethyl acrylate (HEA), and maleic anhydride (MA) by means of free-radical polymerization in an aqueous solution. The morphology and structure of the samples were characterized through scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectrometry, and 1H nuclear magnetic resonance (1H NMR) spectra. The molecular-weight distribution of APEAA–HEA–MA was determined by the gel permeation chromatography method. APEAA–HEA–MA was used as a green decalciﬁng agent to remove calcium from crude petroleum, and the impact of factors such as monomer ratio, copolymerization time, dosages, and desalination temperature was analyzed. It is found that the decalciﬁcation rate of APEAA–HEA–MA could reach to its maximum, and the calcium removal eﬃciency was approximately 97.88% when the monomer molar ratio of APEAA–HEA–MA was 1:2:5, the reaction time of copolymerization was 2 h, the dosage was 100 ppm, and the desalination temperature was 100 °C. This research work can promote the exploration on facile synthesis of a novel terpolymer and its potential application in reﬁnery desalting processes.

1. INTRODUCTION

In recent years, with the excessive exploitation of many oil ﬁelds, crude petroleum tended to become more and more diﬃcult to process because of the increasing quantities of sour, acidic, and heavy crude petroleum.1 These types of crude oils have a comparatively high content of metal salts. Moreover, with the need for deep processing of crude petroleum and hydrogenation, metals (such as calcium and iron) in crude petroleum would cause particular problems during the reﬁnery process.2 The metal compounds would be quickly deposited on the surface of the catalyst during the catalytic cracking process of raw oil, resulting in catalyst poisoning and losing its activity.3 Calcium in crude petroleum generally exists in the form of calcium naphthenate, calcium phenol, fatty acid calcium, and a handful of inorganic acid calcium salts.4 Most water-soluble inorganic metal salts can be separated from the feedstock by normal processes, such as water washing and desalting, but oil-soluble organic calcium compounds cannot be easily removed by these methods.5 Therefore, some additional processes are needed to remove these compounds. Several techniques have been utilized for the removal of calcium and iron from crude petroleum, such as the hydrodemetalization,6 the solvent extraction,7 the electrochemical deposition method,8 and so forth. However, these techniques require a high investment in the equipment needed for the removal of calcium and iron.11 In addition, the disposal of waste catalysts is also very expensive. Thus, it would be desirable to remove these calcium compounds by adding a decalciﬁng agent during the process of desalting pretreatment.

Until now, various chemical agents have been proposed for their application in removing organic calcium, iron, and other metal compounds in crude petroleum, such as carboxylic acids and carboxylic esters, phosphoric acid and its salts, alkyl phosphate ester and its derivatives, and so forth.12 However, these materials have strongly corrosive and low-eﬃciency problems.12 Moreover, they would cause severe environmental pollution problems. For example, phosphoester can generate insoluble phosphonate complexes, and they can hydrolyze to +

Supporting Information

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yield orthophosphates resulting in the formation of calcium–phosphate deposits in the presence of excess calcium, and phosphorus is the main element to the eutrophication of the water body. Therefore, it is necessary to develop a new environmentally green, phosphate-free, and high-efficiency agent to remove the metal contaminants, especially calcium and iron, from crude petroleum.

The copolymer was developed in the late 1970s because it has a strong multifunctional complexation and excellent polymolecular properties. There are some kinds of highly efficient and low-corrosive polymers that have been used as decalcifying agents, such as poly-glycolic esters and poly hydroxyl-carboxylic acids, during the electro-desalting process in petroleum because of their controllable pH range and different functional groups. Moreover, some of them can be used as a scale inhibitor and a metallic corrosion inhibitor. However, when these polymers were used as a demetallization agent, the required dosage was so large that it would increase the difficulty scale of the treatment of the subsequent wastewater, and a large amount of precipitation in the crude oil will also cause corrosion and scaling of the processing equipment. Hence, it is necessary to develop an environmentally friendly “green” polymer which is amphipathic (hydrophilic and oleophilic) and contains efficient functional groups.

In this article, the allylpolyethoxy amino carboxylate−2-hydroxyethyl acrylate−maleic anhydride (APEAA−HEA−MA) terpolymer was designed as a novel phosphorous-free decalcifying agent for removing calcium from crude petroleum. The influence of reaction temperature, reaction time, and the dosage of decalcifying agent on the decalcifying efficiency was determined. The results demonstrated that the terpolymer of APEAA−HEA−MA had successfully removed calcium from crude petroleum as a highly efficient decalcifying agent.

2. RESULTS AND DISCUSSION

2.1. Fourier Transform Infrared and Nuclear Magnetic Resonance Measurement. The Fourier transform infrared (FT-IR) spectra were taken for allyloxy polyethoxy ether (APEG) (a), APEAA (b), and APEAA−HEA−MA (c), which are presented in Figure 1. It is shown that the 1723 cm\(^{-1}\) strong intensity absorption peak (−C=O) in curve b clearly reveals that APEAA has been synthesized successfully. The bands at 1646 cm\(^{-1}\) are from the stretching of −C=C− groups [it can be seen in curves a and b]. However, there are no peaks between 1620 and 1680 cm\(^{-1}\) in curve c, indicating that the free-radical polymerization among APEAA, HEA, and MA has happened successfully.

The \(^1\)H NMR spectra for APEG (a), APEAA (b), and APEAA−HEA−MA (c, d) were exhibited in Figure 2.

Figure 1. FT-IR spectrums of APEG (a), APEAA (b), and APEAA−HEA−MA (c).

Figure 2. \(^1\)H nuclear magnetic resonance (\(^1\)H NMR) spectra of APEG (a), APEAA (b), and APEAA−HEA−MA (c, d).

(CD\(_3\))\(_2\)SO (\(\delta = 2.53\) ppm) was used as the solvent for \(^1\)H NMR spectra (a−c), and D\(_2\)O (\(\delta = 4.80\) ppm) was used as the solvent for \(^1\)H NMR spectra (d). The protons of characteristic groups such as propenyl protons (\(\delta = 3.88−4.01\) ppm), active hydrogen in APEG (−OH, \(\delta = 4.40−4.60\) ppm), and ether groups (−OCH\(_2\)CH\(_2\)−, \(\delta = 3.10−3.90\) ppm) for APEG, APEAA, and APEAA−HEA−MA were...
different from each other. APEG (Figure 4a): \( \delta = 2.53 \) ppm (solvent residual peak of (CD$_3$)$_2$SO), \( \delta = 3.44, 3.45, 3.54 \) ppm (–OCH$_2$CH$_2$–, ether groups), \( \delta = 3.98 \) ppm (CH$_2$=CH–CH$_2$–, propenyl protons), \( \delta = 4.55 \) ppm (–OH, active hydrogen). APEAA (Figure 4b): \( \delta = 2.53 \) ppm (solvent residual peak of (CD$_3$)$_2$SO), \( \delta = 3.44, 3.54 \) ppm (–OCH$_2$CH$_2$–, ether groups), \( \delta = 3.97 \) ppm (CH$_2$=CH–CH$_2$–, propenyl protons). APEAA–HEA–MA (Figure 4c): \( \delta = 2.53 \) ppm (solvent residual peak of (CD$_3$)$_2$SO), \( \delta = 3.11 \) ppm (–OCH$_2$CH$_2$–, ether groups), \( \delta = 4.41, 4.50 \) ppm (–OH, active hydrogen). APEAA–HEA–MA (Figure 4d): \( \delta = 2.50 \) ppm (–CH$_2$–CH–, methylene protons), \( \delta = 3.37 \) ppm (–OCH$_2$CH$_2$–, ether groups), \( \delta = 4.50 \) ppm (–OH, active hydrogen), \( \delta = 4.80 \) ppm (solvent residual peak of D$_2$O).\(^{26} \) \(^{13} \)C NMR (Figure S3, (CD$_3$)$_2$SO, 600 MHz): \( \delta = 194.92, 167.20, 166.39, 165.47, 164.79, 135.25, 134.41, 132.84, 128.76, 72.81, 71.75, 70.26, 70.05, 69.80, 68.53, 65.43, 64.69, 60.70, 58.51, 40.16, 40.02, 39.88 \) ppm.

Compared with Figure 2a, the disappeared peak at \( \delta = 4.55 \) ppm (–OH, active hydrogen) in Figure 2b indicates that the active hydroxyl group of APEG has reacted with L-ascorbic acid (Figure S1),\(^{27,28} \) which confirms the FT-IR analysis of emerging 1723 cm$^{-1}$ strong intensity absorption peak (–C=O) in Figure 2b. Moreover, the double-bond absorption peaks at \( \delta = 3.97 \) ppm (CH$_2$=CH–CH$_2$–, propenyl protons) in Figure 2b completely disappeared in Figure 2c because of the free-radical polymerization among APEAA, HEA, and MA. From the analysis of FT-IR and $^1$H NMR spectra, it can be concluded that the structure of synthesized APEAA–HEA–MA satisfied the expected requirements.

### 2.2. Morphology of the Terpolymer

Figure 3 showed the scanning electron microscopy (SEM) (a,b) and transmission electron microscopy (TEM) (c,d) images of APEAA–HEA–MA terpolymer. It can be seen from the images that the morphology of the terpolymer was catenulate with twig. The structure resembling the crab’s pincers makes it easy for APEAA–HEA–MA terpolymer to contact with the compound organic calcium (calcium naphthenate, phenylcalcium, etc.) and form amphipathic (hydrophilic and oleophilic) chelate between APEAA–HEA–MA and calcium ions.\(^{29} \)

### 2.3. Molecular-Weight Determinations by GPC

Figure 4 displayed the molecular-weight distribution of APEAA and APEAA–HEA–MA. As can be seen, the curve of response to retention time is unimodal, and the molecular weight shows the infinitely uniform distribution.\(^{30} \) According to the analysis of GPC information, the number-average molecular weight (\( M_n \)) and the weight-average molecular weight (\( M_w \)) of APEAA are 1140 and 1942, respectively, and for APEAA–HEA–MA, the number-average molecular weight (\( M_n \)) and the weight-average molecular weight (\( M_w \)) are 2687 and 4026, respectively, and the polydispersity index (\( \text{PID} = M_w/M_n \)) of APEAA and APEAA–HEA–MA are 1.7035 and 1.4983, respectively. In addition, the molecular weight and the molecular-weight distribution would be influenced by the reaction time of copolymerization and would impact the calcium removal ability. The molecular mass and the molecular-weight distribution were determined by GPC (Table 1).

| entry | reaction time (h) | \( M_n \) | \( M_w \) | \( \text{PID} \) |
|-------|------------------|----------|----------|----------------|
| 1     | 0.5              | 1139     | 895      | 1.2726         |
| 2     | 1.0              | 1207     | 963      | 1.2534         |
| 3     | 1.5              | 1504     | 1458     | 1.0316         |
| 4     | 2.0              | 4026     | 2687     | 1.4983         |
| 5     | 2.5              | 6853     | 4283     | 1.6001         |
| 6     | 3.0              | 17,051   | 9472     | 1.8001         |

\(^{a}\)Weight-average molecular weight. \(^{b}\)Number-average molecular weight. \(^{c}\)Polydispersity index, \( M_w/M_n \).
molecular-weight distribution might perform better for calcium removal.

2.4. Effect of Molar Ratio of APEAA−HEA−MA on Decalcification Efficiency. Figure 5a demonstrates the decalcification efficiency of APEAA−HEA−MA with different monomer molar ratios (dosage: 100 ppm; desalination temperature: 100 °C), and the calcium content of the crude petroleum after electric desalting and the electric desalting water is exhibited in Figure 5b. The conversion rate, ratio of functional groups, and the sequence structure of the polymer will all be variable because of the different molar ratios. Only when the proportion of the functional groups are appropriate, the polymers would have a good performance of removing calcium from crude petroleum because the different compounds and structures of the polymers obviously have an influence on the gravitation and repulsion to particles. As can be seen from the data exhibited in Figure 5a, the molar ratio of APEAA−HEA−MA had an influence on the decalcification of APEAA−HEA−MA, and when the molar ratio of APEAA−HEA−MA was 1:2:5, the APEAA−HEA−MA terpolymer exhibited a superior calcium removal efficiency; hence, we decided to choose a monomer molar ratio of 1:2:5 for the further research.

Figure 5. (a) Influence of molar ratio of APEAA−HEA−MA on decalcification efficiency, and (b) calcium material balance after electric desalting.

Figure 6. (a) Effect of reaction time of copolymerization on the calcium removal efficiency, and (b) calcium material balance after electric desalting.

Figure 7. (a) Effect of dosage of APEG, APEAA, and APEAA−HEA−MA on the decalcification efficiency, and (b) calcium material balance for APEAA−HEA−MA (1:2:5) after electric desalting.
2.5. Influence of Copolymerization Time of APEAA–HEA–MA on Decalcification Efficiency. The experiments were to study the patterns of how copolymerization time affected the calcium removal efficiency when taking APEAA–HEA–MA (1:2:5) as a decalciﬁing agent (dosage: 100 ppm and desalination temperature: 100 °C), and the results are shown in Figure 6. It can be found that the removal efficiency of calcium for APEAA–HEA–MA (1:2:5) is 55.29% when the copolymerization time is 0.5 h. As can be seen, the removal efﬁciency of calcium for the APEAA–HEA–MA (1:2:5) terpolymer increases to 97.88% when the copolymerization time is increased up to 2 h. This result may attribute to that the increase of copolymerization time could make the terpolymer proportions of the functional groups in long-chain macro-molecules appropriate and enhance its decalcifying property. However, the APEAA–HEA–MA (1:2:5) sample exhibited a significant decrease in calcium removal efﬁciency when the copolymerization time is increased up to 2 h. Therefore, the different reaction times of copolymerization could cause the different extents of reaction and degree of polymerization of the APEAA–HEA–MA, and these results illustrated that the terpolymer of APEAA–HEA–MA displayed the best efﬁcacy of decalcification from the crude petroleum with 2.0 h of the copolymerization time.

2.6. Effect of Dosage of APEAA–HEA–MA on Decalcification Efficiency. Figure 7a exhibited the data of decalcification efﬁciency with adding several dosages of APEG, APEA, and APEAA–HEA–MA under 100 °C, and the calcium material balance for APEAA–HEA–MA (1:2:5) after electric desalting was displayed in Figure 7b. The decalcification efﬁcacy was only 11.48% without adding any chemical additive to crude petroleum. However, when the terpolymer APEAA–HEA–MA (1:2:5) was added into the oil, the decalcification could be increased quite signiﬁcantly, achieving 97.88% when the dosage of APEAA–HEA–MA (1:2:5) was up to 100 ppm. Comparatively, APEG and APEA could only approach 20.01 and 25.38%, respectively, under the same condition. Because APEAA–HEA–MA (1:2:5) contains more carboxyl (−COOH), amino (−NH₂), and ester groups (−COO−) and the synergistic effect between them, the terpolymer shows the best calcium removal efﬁciency. However, the decalcification efﬁcacy does not obviously increase correspondingly when the concentration of APEAA–HEA–MA (1:2:5) exceeds 100 ppm. Comparatively, the APEAA–HEA–MA terpolymer performs extremely effectively in calcium removal and lowers the calcium content by using a small dosage during desalting to render a higher-quality crude oil.

2.7. Influence of Desalination Temperature on Decalcification Efficiency. The results of using APEAA–HEA–MA (1:2:5) as a decalciﬁing agent (dosage: 100 ppm) under different desalination temperatures are presented in Figure 8a, and the calcium content in electric desalting water and crude petroleum after electro-desalting is shown in Figure 8b. It can be seen from the data that the decalciﬁcation rate of APEAA–HEA–MA (1:2:5) is 44.18% when the desalination temperature is 60 °C. However, the removal efﬁciency of calcium for the terpolymer of APEAA–HEA–MA increased to 97.88% when the temperature reached 100 °C. This phenomenon can be ascribed to the higher temperature and could give the terpolymer enough energy to make the functional groups more active and raise its decalcifying ability. However, when the temperature was risen from 120 to 180 °C, there was an obvious decrease in the calcium removal efﬁciency for the APEAA–HEA–MA terpolymer. When the temperature is at that high, the water evaporation is much faster than droplet coalescence, and the hydrolysable calcium compounds could barely separate from the crude petroleum into the desalting water. As can be seen, the optimum temperature was 100 °C, and the decalciﬁcation efﬁciency could reach up to 97.88%.

2.8. Comparison with Other Polymers. The decalciﬁcation property of the APEAA–HEA–MA (1:2:5) terpolymer was compared with several commercial phosphorous-free polymers under the desalination temperature of 100 °C, and the data are shown in Figure 9. As can be seen from Figure 9, the decalciﬁcation ability followed the order of APEAA–HEA–MA > hydrolyzed polymaleic acid (HPMA) > polyacrylic acid (PAA) > polyepoxysuccinic acid (PESA). In particular, the decalciﬁcation rate of the APEAA–HEA–MA (1:2:5) terpolymer could reach 97.88% at the dosage of 100 ppm, whereas HPMA, HPMA, and PESA could only reach 26.86, 31.28, and 20.09%, respectively. Furthermore, when the volume of addition for APEAA–HEA–MA (1:2:5) exceeded 100 ppm, the decalciﬁcation rate remains basically unchanged with the increase of dosage. However, HPMA, PAA, and PESA also exhibit a relatively excellent calcium removal property from crude petroleum, with 66.83, 59.92, and 54.27% at a dosage of 250 ppm, respectively. Even more, PESA performs better decalciﬁcation property than both HPMA and PAA when the dosage exceeded 300 ppm. The superior effectiveness exhibited by APEAA–HEA–MA terpolymer is provided by
the presence of amino (−NH₂), carboxyl (−COOH), and ester groups as active sites and their synergistic effect. The terpolymer of APEAA−HEA−MA performs extremely better on the calcium removal capability compared to other chemical additives, such as HPMA, PAA, and PESA. In addition, the cost of decalcification agents is also an important factor affecting its application, and the cost of APEAA−HEA−MA was contrasted with other typical polymers of PAA, HPMA, and PESA. As shown in Table 2, it can be found that the cost of APEAA−HEA−MA terpolymer is a little bit higher than that of other polymers. However, the dosage of APEAA−HEA−MA is much less than that of other polymers in practical application because of its excellent decalcification performance. Therefore, the APEAA−HEA−MA terpolymer would have a relative lower cost, and it might produce higher economic benefit as a potential decalcifying agent of crude oil.

3. CONCLUSIONS
In summary, the APEAA−HEA−MA terpolymer had an excellent performance on the removal of calcium from crude oil with a low reagent/oil mass ratio. The effect of reaction conditions on the decalcification performance was studied systematically. Briefly, the terpolymer had an excellent decalcification performance when the proportion of functional groups are carefully designed and adjusted, which has been ascribed to the different functional groups and structures of the terpolymer that could influence on the gravitation and repulsion to particles. The different molecular weights and molecular-weight distributions determined by the copolymerization time influence the solubility and stability of the terpolymer and therefore its decalcification performance. An increase in the desalination temperature could make the functional groups more active and so increase its decalciying ability. However, further increases above 120 °C would restrain water droplets to coalesce, and the hydrosoluble calcium compounds could barely separate from the crude petroleum rapidly enough. Therefore, appropriate molar ratio, molecular weight, dosage, and desalination temperature are key parameters for reaching the maximum decalcification rate at the minimum cost. At last, when the APEAA−HEA−MA terpolymer was used as a reagent and the reaction conditions were at the monomer molar ratio (APEAA−HEA−MA) of 1:2:5, the copolymerization reaction time of 2.0 h, the dosage of 100 ppm, and the desalination temperature of 100 °C, the decalcification rate could reach 97.88%. Compared with other nonphosphorus polymers such as HPMA, PAA, and PESA, APEAA−HEA−MA containing more amino, carboxyl, and ester groups displays the best calcium removal ability from crude petroleum. On the basis of the above results, APEAA−HEA−MA is an efficient decalcifying agent for crude petroleum.

4. EXPERIMENTAL SECTION
4.1. Materials. APEG (M_w = 400 g·mol⁻¹), L-aspartic acid (M_w = 133.10 g·mol⁻¹), 2-HEA (M_w = 116.12 g·mol⁻¹), MA (M_w = 98.06 g·mol⁻¹), and ammonium persulfate (APS, M_w = 228.201 g·mol⁻¹) were analytically of pure grades and purchased from Aladdin Chemical Regent Co., Ltd. (Shanghai, China). PAA (M_w = 1800 g·mol⁻¹), HPMA (M_w = 600 g·mol⁻¹), and PESA (M_w = 1000 g·mol⁻¹) were of technical grade and supplied by Jiangsu Jianghai Chemical Co., Ltd. (Changzhou, Jiangsu, P. R. China). Distilled water was used for all the studies.

4.2. Preparation of APEAA. As shown in Figure 10, the esterification of the surface hydroxyl groups of APEG was realized with L-aspartic acid according to our previous works. Typically, 0.1 mol of L-aspartic acid was dissolved into 30 mL of water (pH = 3), and the above L-aspartic acid solution was loaded into a three-necked flask, which was placed in the microwave reactor (MCR-3, 900 W). Then, 0.1 mol of APEG was added into the L-aspartic acid solution. Subsequently, the temperature was set to 90 °C and kept at this temperature for 10 min. After cooling to room temperature, the sample of APEAA was obtained.

![Figure 10. Preparation of APEAA.](image-url)

Table 2. Comparison of Cost for Different Polymer Decalcifying Agents

| decalcifying agent | cost (RMB, yuan/ton) |
|--------------------|---------------------|
| PESA               | 8900                |
| PAA                | 7800                |
| HPMA               | 8100                |
| APEAA−HEA−MA (1:2:5)| 9150                |

![Figure 9. Comparison of decalcification efficiency among several polymers.](image-url)
4.3. Preparation of APEAA–HEA–MA. The synthetic process was as follows: 0.01 mol of APEAA was dissolved into 35 mL of water in a 250 mL four-neck round-bottom flask, equipped with a thermometer and a magnetic stirrer. The solution was heated to 75 °C with stirring under a nitrogen atmosphere. Subsequently, solution A including 0.02 mol of HEA, 0.05 mol of MA, and 18 mL of distilled water (the molar ratio of APEAA, HEA, and MA was 1:2:5) and solution B obtained by adding 3.98 g of APS into 18 mL of distilled water were added into the APEAA solution separately at constant flow rates over a period of 2.0 h. After cooling to room temperature, an aqueous solution was added to dissolve the ash. The mixture was maintained in a constant temperature at 100 °C for 10 min to make the APEAA–HEA–MA terpolymer was added into the sample bottle, fixed in the electronic oscillator, and vibrated for 200 times to mix the additives and oil thoroughly. The mixture was then placed in a constant temperature bath at 100 °C for about 30 min for oil–water separation under the action of electric field. Finally, the mixture was maintained in a constant temperature at 100 °C for about 20 min and then cooled to room temperature. The amounts of calcium in crude petroleum were then analyzed. Comparative experiments of using the APEAA, PAA, HPMA, and PESA samples to remove calcium from crude petroleum were also carried out.

4.6. Measuring the Calcium Content in Crude Petroleum. Crude petroleum (10.00 g) was weighed into a DPY-2 electric desalter (ICP-MS, Thermo Elemental X7 Series). The supporting information was added to the oil sample and stirred for 2 min at a high stirring rate (about 2000 rpm) and then the mixed crude petroleum was transferred into a sample bottle which equipped with electrodes. Subsequently, the desired dose of the APEAA–HEA–MA terpolymer was added into the sample bottle, fixed in the electronic oscillator, and vibrated for 200 times to mix the additives and oil thoroughly. The mixture was then placed in a constant temperature bath at 100 °C for 10 min to make the APEAA–HEA–MA terpolymer react with Ca2+ completely. After that, the sample bottle was placed in an electric field for 30 min for oil–water separation. The amounts of calcium in crude petroleum were then analyzed. Comparative experiments of using the APEAA, PAA, HPMA, and PESA samples to remove calcium from crude petroleum were also carried out.

Table 3. Properties of Pipeline Oil Sample

| item                  | value  |
|-----------------------|--------|
| \( \rho_{20} \) g cm\(^{-3} \) | 0.8658 |
| \( v_{50} \) mm\(^3\) s\(^{-1} \) | 12.97  |
| water, wt %           | 1.3    |
| \( C_a \) µg g\(^{-1} \) | 24.4   |
13C NMR spectra of APEA–HEA–MA (PDF)

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**Notes**
The authors declare no competing financial interest.

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