General Strategy for Making CO₂-Switchable Polymers

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S *Supporting Information*

ABSTRACT: By discovering that poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) in water can react with carbon dioxide (CO_2) and have its lower critical solution temperature (LCST) reversibly tuned by passing CO_2 and argon (Ar) through the solution, we describe a general strategy for imparting a CO_2-switchable LCST or water solubility to polymers of broad interest like poly(*N*-isopropylacrylamide) (PNIPAM) and poly[2-(2-methoxyethoxy)ethyl methacrylate] ($PMEO_2MA$). We show that by easy copolymerization incorporating DMAEMA as a CO_2-responsive trigger into PNIPAM or $PMEO_2MA$, their LCST can effectively be switched by the gases. Two examples of

applications were further demonstrated: upon CO_2 or Ar bubbling at a constant solution temperature, hydrogels could undergo a reversible volume transition and block copolymer micelles could be dissociated and reassembled. This study opens the door to a wide range of easily accessible CO_2-switchable polymers, enabling the use of CO_2 as an effective trigger for smart materials and devices.
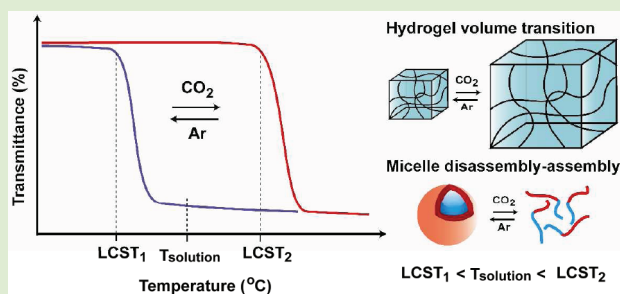
Carbon dioxide (CO_2) is nontoxic, inexpensive, abundant, and an environmentally friendly chemical reagent. Valorizing the use of CO_2 in chemistry is of great and growing interest.[1,2] Switchable solvents and surfactants developed by Jessop's group are a primary example.[3,4] Switching between a hydrophilic and a hydrophobic form upon reaction with CO_2 and its removal, they are useful for green chemical processes such as extraction of organic solvents without distillation[5] and destabilization of colloidal polymer latexes without adding chemicals.[6] Most of them are molecules containing an amidine functionality that can react with CO_2 and water to form a charged amidinium bicarbonate and be recovered upon CO_2 removal.[3–6] Some hydrophobic tertiary amine solvents could also react with CO_2 and become soluble in water.[7] In addition to green chemistry, the use of CO_2 as a trigger for switching property or function of materials may also hold promise for applications. Despite the great interest, there have been very few reports on CO_2-switchable polymers to date. Weiss et al. reported gelation of organic solvents by polyallylamine in the presence of CO_2.[8] Taton et al. investigated the reaction of poly(*N*-heterocyclic-carbene)s with CO_2 and its use in organocatalysis.[9] In another recent report, Yuan et al. designed an amphiphilic diblock copolymer composed of poly(ethylene oxide) (PEO) and a polyacrylamide bearing an amidine side group and found that its self-assembled vesicle could undergo a reversible volume expansion and contraction upon exposure to CO_2 and Ar, respectively.[10] Although incorporating the amidine functionality into a polymer structure represents a general means to render the polymer CO_2-responsive, the synthesis is demanding and the amidine-containing polymers may be hydrolytically unstable.[7] There is a need for more general,

robust, and efficient approaches to enable the use of CO_2 as a trigger for a broad range of polymers and materials.

Herein we report such a strategy based on our discovery that poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA) can react directly with CO_2 in water without functionalization with amidine, which can increase drastically its lower critical solution temperature (LCST), characterizing the transition from a soluble (hydrated) to an insoluble (dehydrated) state.[11] The change in LCST is reversible upon removal of CO_2 using Ar. We thus propose to incorporate DMAEMA or similar amine-containing monomer units into non-CO_2-responsive, thermosensitive polymers of broad interest like poly(*N*-isopropylacrylamide) (PNIPAM)[12] and poly[2-(2-methoxyethoxy)ethyl methacrylate] ($PMEO_2MA$)[13] to render them responsive to CO_2 as well. We show that by easy copolymerization with DMAEMA or other CO_2-reactive units acting as the trigger, PNIPAM and $PMEO_2MA$ can exhibit a CO_2-switchable LCST. Because LCST is the key property exploited in developing thermoswitchable polymers and their smart materials in such forms as microgel, nanogel, micelle, and vesicle,[11–16] an easy way to impart a CO_2-switchable LCST to many polymers makes it possible to use CO_2 to trigger reversible structural changes of smart materials. We demonstrate two examples with (1) a hydrogel that could undergo an isothermal reversible volume transition and (2) a diblock copolymer micelle that could be reversibly dissociated and reassembled by passing CO_2 and Ar through the solution. The principle of using the CO_2-switchable LCST to induce the

structural transitions of hydrogels and micelles at a given solution temperature between the two LCSTs is schematically illustrated in Figure 1. By unveiling this general, simple, and
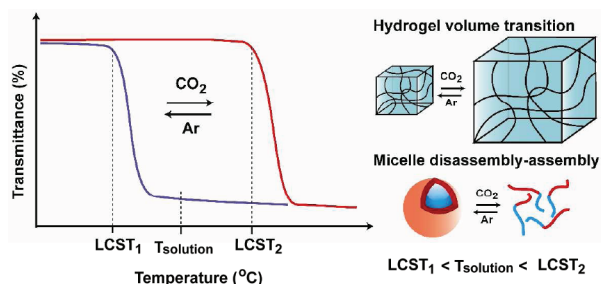
Figure 1. Schematic illustration of the CO_2-switchable LCST and its application for reversible isothermal volume transition of hydrogels and dissociation-assembly of block copolymer micelles.

efficient approach, this study makes the door wide open for accessing a broad range of CO_2-switchable polymers, block copolymers, and their materials.

A number of homopolymers, random copolymers, and block copolymers were synthesized, and their characteristics are given in Supporting Information (Table S1). PDMAEMA dissolved in water displays a LCST around 40 °C[17] and copolymerization with a stimuli-responsive monomer is an effective way to shift its LCST by stimuli.[18] We initially designed a PDMAEMA containing comonomer units of acroylimide whose structure is similar to amidine and should be CO_2-responsive. After bubbling CO_2 through a polymer solution, ^{1}H NMR spectra revealed that not only acroylimide but also DMAEMA units have reacted with CO_2 and water, with a downfield shift of their resonance peaks indicating the formation of bicarbonate salts of protonated amine groups (Figure S1).[7] Thanks to this observation, we realized that PDMAEMA is CO_2-responsive on its own. We thus conducted experiments to see if the LCST of a PDMAEMA sample (Table S1) could be switchable with CO_2 and Ar. As seen from Figure 2a, the solution transmittance measurements indicate the hydration-dehydration transition occurring at about 36 °C, as revealed by the drop of transmittance (cloud point). After 30 s of room temperature CO_2 bubbling at a rate of ~60 mL/min, the cloud point rose drastically appearing at ~64 °C; while after a 5 min purge with CO_2, no cloud point could be detected as the polymer became totally soluble in water over the range of temperatures for the transmittance measurement (from 20 to 90 °C). Subsequently, by passing Ar through the CO_2-treated solution at a similar rate, the LCST decreased upon CO_2 removal and got back to ~56 °C after 2 min of Ar bubbling and recovered completely to the initial value after 10 min. Figure 2b shows photographs of the PDMAEMA solution at 50 °C after CO_2 bubbling (below LCST, transparent) and after purge with Ar (above LCST, opaque), showing the efficient gas-switchable water solubility of the polymer due to the reversible shift of LCST. Figure 2c shows representative ^{1}H NMR spectra of the polymer solution in D_2O before CO_2, after CO_2, and after Ar bubbling at room temperature. Upon CO_2 treatment, the resonance peaks of PDMAEMA (e.g., protons of methyl groups linked to the tertiary amine group at 2.4 ppm) display downfield shift, the extent of which is a function of the reaction time. Upon Ar bubbling, the shift of those resonance peaks was reversed and the initial spectrum of PDMAEMA was recovered. The reaction of PDMAEMA with CO_2 results in protonation of the amine
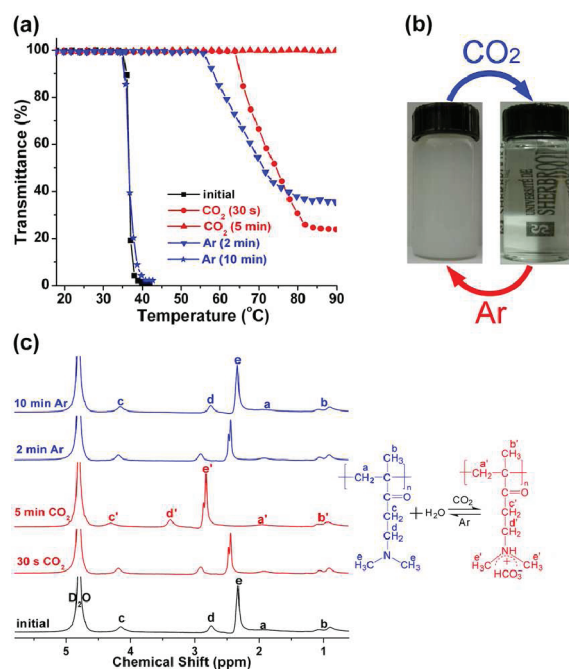

Figure 2. (a) Transmittance (measured at 700 nm) vs temperature for a PDMAEMA aqueous solution (2.0 mg/mL) before CO_2, after CO_2, and after Ar bubbling through the solution. (b) Photographs of the solution at 50 °C after passing CO_2 or Ar through the solution. (c) ^{1}H NMR spectra of PDMAEMA in D_2O recorded before and after passing CO_2 or Ar through the solution at different times.

groups by carbonic acid, forming charged and more water-soluble ammonium bicarbonates.[7] The formation of carbonic acid was accompanied by a pH change. The pH value of the initial polymer solution in Figure 2 was about 7.8; it changed to 5.5 and 4.9 after 30 s and 5 min CO_2 bubbling, respectively, and subsequently was recovered to 6.3 and 7.6 after Ar was passed through the solution for 2 and 10 min, respectively. The LCST increases because the presence of more hydrophilic como-nomer units in a LCST-polymer has an effect of raising the phase transition temperature.[19] The ^{1}H NMR spectral change is similar to the effect of protonation upon addition of a strong acid like HCl.[20,21] The results in Figure 2 show that the LCST of PDMAEMA can be reversibly switched between two temperatures (Figure 1) by using CO_2 and Ar as triggers. Moreover, by limiting the amount of CO_2 going through the solution, which is possible by adjusting the flow rate or the bubbling time (like in Figure 2), PDMAEMA could be partially protonated, yielding a statistical copolymer with protonated and nonprotonated amine groups. As the protonation degree determines the shift of LCST, this could allow the extent of the LCST shift to be reversibly tuned. Although changing the pH of an aqueous solution of PDMAEMA has a similar effect on the LCST, the interest here is the use of removable gases (CO_2 and Ar) to trigger the switching process instead of adding acids or bases into the solution.

PDMAEMA is a weak polybase widely used in designing thermosensitive materials based on its LCST. The discovery of its efficient reaction in water with CO_2 means that many CO_2-responsive materials can now be formulated with the use of PDMAEMA. But more important is that DMAEMA can easily be copolymerized with many types of non-CO_2-responsive polymers and act as a CO_2-sensitive trigger to render them also responsive to CO_2. Moreover, the CO_2 responsiveness of
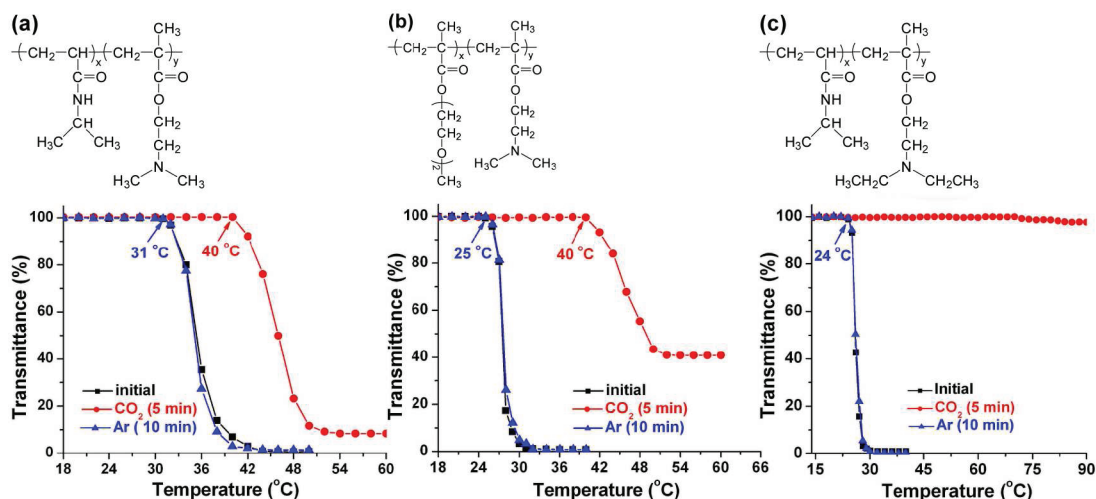
Figure 3. Transmittance vs temperature for aqueous solutions of three random copolymers (2 mg/mL): (a) P(NIPAM-*co*-DMAEMA) (4 mol % of DMAEMA), (b) P(MEO2MA-*co*-DMAEMA) (6 mol % of DMAEMA), and (c) P(NIPAM-*co*-DEAEMA) (16 mol % of DEAEMA). All solutions were subjected to 5 min of CO_2 and 10 min of Ar bubbling.
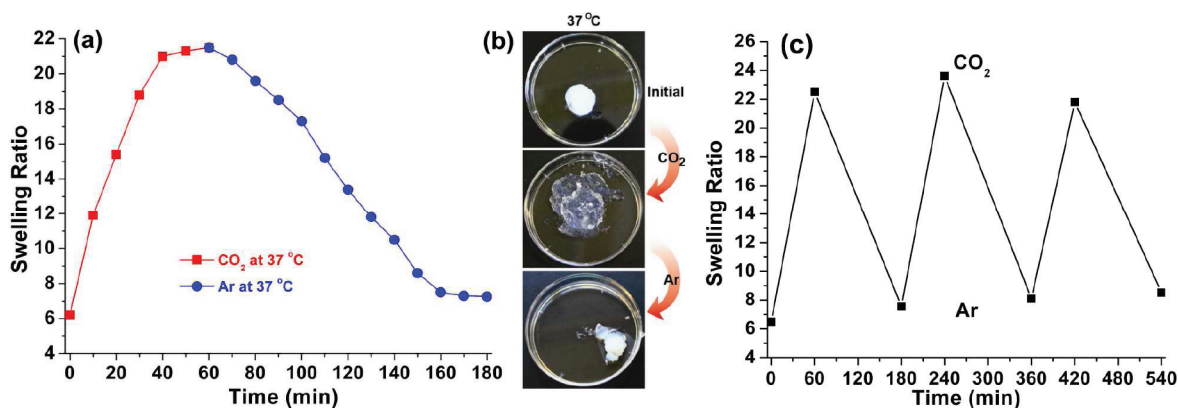
Figure 4. (a) Change in the swelling ratio over time for a hydrogel of P(NIPAM-*co*-DMAEMA) at 37 °C under CO_2 (swelling) and Ar bubbling (deswelling). (b) Photographs of the hydrogel equilibrated at 37 °C, after 1 h of CO_2 bubbling and 2 h of Ar bubbling through the solution. (c) Reversible change in the swelling ratio at 37 °C upon three cycles of CO_2 (1 h) and Ar (2 h) bubbling.

PDMAEMA should be found with many other amine-containing polymers, such as poly(*N,N*-diethylaminoethyl methacrylate) (PDEAEMA). To test the generality and versatility in making polymers with a CO_2-switchable LCST, we investigated a number of random copolymers. Figure 3 shows the results obtained with three copolymers. The first two are PNIPAM and PMEO$_2$MA containing about 4 and 6 mol % of DMAEMA, respectively, and the third one is PNIPAM with 16 mol % of DEAEMA units. PNIPAM and PMEO$_2$MA were chosen because they are representative examples of two important classes of polymers displaying a LCST in water.[12,13] In all cases, the cloud point temperature increased after CO_2 and was recovered completely after Ar bubbling. Despite a low concentration of DMAEMA, the CO_2-induced LCST shift is ~9 °C for P(NIPAM-*co*-DMAEMA) (Figure 3a) and 15 °C for P(MEO$_2$MA-*co*-DMAEMA) (Figure 3b). As for P(NIPAM-*co*-DEAEMA) containing a greater amount of DEAEMA, it became much more soluble in water, and the LCST is hardly discernible after CO_2 bubbling (Figure 3c). Obviously the amount of CO_2 trigger is important in determining the LCST increase upon reaction with CO_2. For PNIPAM and PMEO$_2$MA with ~25 mol % of DMAEMA (Table S1), no LCST could be observed after CO_2 bubbling.

^{1}H NMR spectra revealed the reversible protonation of DMAEMA or DEAEMA units in these copolymers, while NIPAM or MEO$_2$MA units were not affected by CO_2 (Figures S2−S4). These results thus confirmed that incorporating amine-containing comonomer units (DMAEMA or DEAEMA) as a CO_2-sensitive trigger into LCST polymers (PNIPAM and PMEO$_2$MA) is an easy way to provide these polymers with a CO_2-switchable LCST or water solubility.

For thermosensitive polymers like PDMAEMA, PNIPAM, and PMEO$_2$MA, their transition from a soluble to an insoluble state upon heating, or the reversed transition on cooling, is the basis for many smart materials and applications. Examples include the thermally induced reversible volume transition of bulk, micro-, or nanosized hydrogels[12−16] and temperature-controlled self-assembly or disassembly of polymer micelles or vesicles.[22−24] The effective and reversible shift of LCST by exposure to CO_2 and Ar suggests numerous possibilities of developing materials switchable with CO_2 at a constant temperature. To test this, we performed experiments on two systems. On the one hand, we synthesized a bulk hydrogel based on a cross-linked random copolymer of P(NIPAM-*co*-DMAEMA) (Supporting Information). Indeed, the large shift of LCST made it possible to achieve an isothermal reversible

volume transition of the hydrogel triggered by passing CO_2 and Ar through the aqueous solution. Figure 4a shows the results obtained at 37 °C (body temperature). A piece of the hydrogel
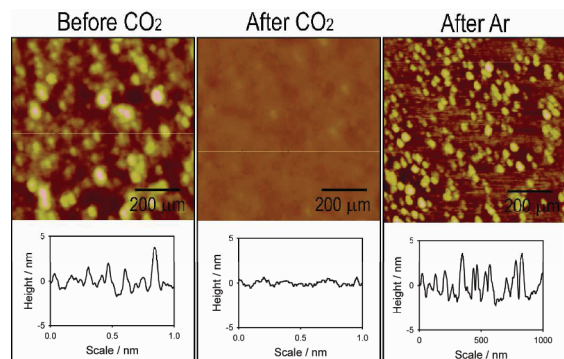
Figure 5. AFM height images for samples cast from an aqueous solution of PEO$_{45}$-*b*-P(NIPAM$_{220}$-*co*-DEAEMA$_{90}$) at 40 °C before CO_2, after CO_2 bubbling, and after Ar bubbling through the solution. The height profiles correspond to the marked lines in the images.

equilibrated at 37 °C (T > LCST) had a swelling ratio (SR) of about 6 (SR is the ratio of the weight of absorbed water to the weight of the dried gel). When CO_2 was bubbled through the solution at a rate of about 60 mL/min, the gel started to swell due to the shift of the LCST to above 37 °C, with SR reaching 21 after 1 h. When purged with Ar, the gel started to deswell because the LCST was shifted to below 37 °C again, with SR recovering to about 7 after 2 h. The deswelling rate appears to be slower than the swelling process. Figure 4b shows photographs of the piece of hydrogel at 37 °C (top view) before CO_2, after 1 h of CO_2 bubbling, and after 2 h of Ar bubbling, showing the reversible gas-induced volume transition. This isothermal volume transition was reversible, as seen from Figure 4c, showing the switching SR of the hydrogel for three cycles of CO_2 (1 h) and Ar (2 h) exposures (a new piece of gel was utilized for this experiment). The achievable deswelling degree seems to decrease slightly over time, but the differences are essentially within experimental error and, in addition, the hydrogel was not optimized for switching performance. The slow swelling and deswelling kinetics are partly due to the large size of bulk hydrogels. It is expected that, with micro- or nanogels, the CO_2-switchable volume transition should be faster. Moreover, various experimental conditions could affect the reaction rate of DMAEMA groups with CO_2 and the rate of CO_2 removal by Ar, which include the rate of gas flow, size of the gel, solution volume, and temperature.

On the other hand, we synthesized a diblock copolymer of PEO-*b*-P(NIPAM-*co*-DEAEMA) (Table S1). It was soluble in water at room temperature, which is below the LCST of the P(NIPAM-*co*-DEAEMA) block (∼ 33 °C) and self-assembled into micelles upon heating the solution to T > LCST as the P(NIPAM-*co*-DEAEMA) block became hydrophobic. By passing CO_2 through the micellar solution at 40 °C, as the LCST of the P(NIPAM-*co*-DEAEMA) block increased to above the solution temperature, which can be observed from variable-temperature ^{1}H NMR measurements (Figure S6), the micelle core formed by the P(NIPAM-*co*-DEAEMA) block was dissolved. After purging with Ar, as the LCST was shifted to below the solution temperature again, micelles were reassembled. This isothermal gas-induced dissociation and reassembly of the micelles is visible from AFM observations.

Figure 5 shows AFM height images obtained by casting the micelle solution at 40 °C. In the initial solution, micellar aggregates (43 ± 9 nm) were formed; after CO_2 bubbling, the micelles basically disappeared completely, and the height profile of the AFM image indicates a flattened film; after passing Ar through the transparent solution, micellar aggregates (39 ± 5 nm) reappeared. For the micellar aggregates, both before purge with CO_2 and after purge with Ar, the apparent low heights (∼5 nm) imply that micelles were not spherical, likely due to a dense packing and collapse during drying of the samples. Dynamic light scattering (DLS) measurements found an average hydrodynamic diameter of about 67 nm for the initial micelles and 46 nm for the micelles after reassembly upon Ar bubbling, which, qualitatively, is consistent with the AFM images for dried micelles. TEM observations also indicated the formation of micelles as well as their dissociation and reformation after purge with CO_2 and Ar, respectively (Figure S7). This CO_2-induced reversible dissociation of block copolymer micelles could be observed for all systems where the LCST of one block controls the formation of micelle core or vesicle membrane. It is to be noted that in the present case, the block copolymer micelles were completely dissociated upon CO_2 bubbling, which differs from the volume change of block copolymer vesicles[10] and from the permeability switch of a polyelectrolyte microcapsule whose CO_2-responsiveness came from an oligoamine doped in the microcapsule wall.[25]

To conclude, we reported the discovery that PDMAEMA in water can react with CO_2 through the side amine groups, which has the effect of increasing the LCST. By controlling the protonation degree by CO_2 and Ar bubbling, the LCST can be reversibly tuned and switched. On the basis of this finding, we described and demonstrated a general strategy that makes the making of polymers with a CO_2-switchable LCST easily accessible. It consists in incorporating DMAEMA or other amine-containing units like DEAEMA as a CO_2-sensitive trigger into the structures of non-CO_2-responsive thermosensitive polymers such as PNIPAM and PMEO$_2$MA. Because LCST is the property of enormous scientific and technological interest, its easy control by the gases offers numerous possibilities to develop CO_2-switchable smart materials. We demonstrated two examples with a bulk hydrogel of P(NIPAM-*co*-DMAEMA) and block copolymer micelles of PEO-*b*-P(NIPAM-*co*-DEAE-MA). Triggered by passing CO_2 and Ar through the solution at a constant temperature, the hydrogel could undergo a reversible volume transition while the micelles could be dissociated and reassembled due to the CO_2-switchable LCST or water solubility. The discovery made and the strategy demonstrated in this study open the door to a wide range of easily accessible CO_2-switchable polymers. This is important for valorizing CO_2 in polymer and materials chemistry and may enable the use of CO_2 as a trigger to switch the structures or functions of a variety of smart polymer materials and devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Polymer syntheses and more characterization results using ^{1}H NMR, TEM, and solution transmittance measurements. 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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