

Synthesis of polydisulphide via iodine oxidation for self-healing applications

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Abstract:

Self-healing materials with scratch-healing capabilities have garnered significant attention in recent years. Among the various reversible bonds investigated as healing mechanisms in polymer materials, dynamic disulphide chemistry has been particularly appealing. This study reports the synthesis of a polydisulphide as a healing segment, incorporating reversible disulphide bonds for self-healing applications. The polydisulphide was synthesised through the oxidation of a telechelic mercaptan compound, employing iodine as the oxidising agent. The resulting polydisulphide was characterised by proton nuclear magnetic resonance (¹H NMR) and Fourier transform infrared spectroscopy (FT-IR). It was then crosslinked with telechelically acrylate end-capped polycaprolactone and a tetrathiol crosslinker via the thiol-acrylate Michael addition reaction, forming a self-mendable network. The network was further characterised using FT-IR, differential scanning calorimetry, optical microscopy, and tensile testing. Optical microscopy confirmed the network's scratch-healing ability, while tensile testing demonstrated a strength recovery of 62% after scratching and subsequent healing at 100°C for 24 hours.

Keywords: iodine, Michael thiol-acrylate addition, polydisulphide, self-healing.

Classification numbers: 2.1, 2.2, 2.3

1. Introduction

Self-healing materials capable of repairing scratches upon activation have attracted considerable attention over the past decades [1]. Numerous strategies have been developed to create self-healing materials by incorporating healing agents (extrinsic systems) or reversible bonds (intrinsic systems) into network structures [2-6]. Among the extensively explored reversible bonds, the disulphide bond has been of particular interest [7]. This bond is reversible, as it can dissociate to form sulphenyl radicals that re-associate [7]. Additionally, disulphide bonds can undergo exchange reactions, making them reliable as healing mechanisms. Several reports detail self-healing materials based on disulphide exchange reactions activated by either heat or UV light [8, 9]. Disulphide bonds have also been incorporated into waterborne polyurethanes to impart self-healing properties [10-12].

Motivated by this, we synthesise a polydisulphide via the oxidation of a telechelic dimercaptan organic compound using iodine, which serves as a cost-effective and low-toxicity catalyst in the aerobic oxidation of thiols.

The polydisulphide is subsequently crosslinked with telechelically acrylate end-capped polycaprolactone and a tetrathiol crosslinker via the thiol-acrylate Michael addition reaction. This novel synthesis route aims to produce disulphide-based materials capable of thermal-triggered scratch healing. Polycaprolactone (PCL), a widely used polyester, serves as a shape-memory segment within the polymer structure. By reacting telechelically acrylate end-capped PCL with polydisulphide and a tetrathiol crosslinker, the resulting polymer network integrates PCL's shape-memory properties. These properties, driven by the melting and crystallisation behaviour of the PCL phase, facilitate crack closure during the healing process.

2. Experimental section

2.1. Materials

2,2'-(ethylenedioxy)diethanethiol (95%) and pentaerythritol tetrakis(3-mercaptopropionate) (tetrathiol, 95%) were purchased from Sigma-Aldrich. Iodine (I₂, 99.5%) was purchased from Fisher. All the solvents (HPLC grade) were purchased from Fisher and used as received. Telechelically

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acrylate end-capped polycaprolactone (PCL-bisacrylate, 8,000 g/mol) was synthesised following the previously reported procedure [13].

2.2. Instrumentation

Proton nuclear magnetic resonance (^1H NMR) spectra were recorded in deuterated chloroform (CDCl_3) with TMS as an internal reference, on a Bruker Avance 300 at 300 MHz. Attenuated total reflectance (ATR) FT-IR spectra were collected as the average of 128 scans with a resolution of 4 cm^{-1} on a FT-IR Tensor 27 spectrometer equipped with a Pike MIRacle ATR accessory with a diamond/ZnSe element. Size exclusion chromatography (SEC) measurements were performed on a polymer PL-GPC 50 gel permeation chromatograph system equipped with an RI detector, with tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 ml/min. Molecular weight and molecular weight distribution were calculated with reference to polystyrene standards. Optical microscopic images were recorded on an Olympus GX51F microscope. Differential scanning calorimetry was recorded on a TA Instruments differential scanning calorimetry 2910 at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen flow. Tensile tests (ASTM D638, 10 mm min^{-1} , three replica specimens were subjected to test for each measurement) were performed using a Tensilon RTC-1210A tensile test machine. For tensile testing of scratch healing, a scratch was introduced at the centre of the specimen along its width.

2.3. Synthesis of polydisulphide using iodine

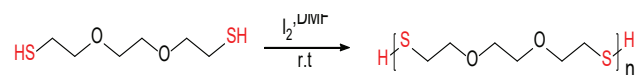
An amount of 2,2'-(ethylenedioxy)diethanethiol (0.182 g, 1 mmol) was dissolved in dimethylformamide. A solution of iodine (0.254 g, 1 mmol, 20 wt%) in dimethylformamide was added dropwise. The reaction was stirred at room temperature for 6 hours. The reaction solution was washed with an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (10 wt%), then extracted with chloroform. The extract was washed with K_2CO_3 and dried under vacuum. Yield: 69%.

2.4. Synthesis of network

Polydisulphide, tetrathiol, and PCL-bisacrylate (molar ratio of polydisulphide:tetrathiol:PCL-bisacrylate=3:1:5) were well-mixed in a minimum amount of tetrahydrofuran as the solvent. Triethylamine (5 mol% of the acrylate groups) as catalyst was then added. After 4 hours, the received raw cured product was dried under vacuum to remove the catalyst and solvent.

3. Results and discussion

3.1. Synthesis of polydisulphide



Scheme 1. Synthesis of polydisulphide.

The monomer 2,2'-(ethylenedioxy)diethanethiol (dithiol) was oxidised in the presence of iodine in dimethylformamide to form polymers containing repeated disulphide units and telechelic thiol end groups (Scheme 1). Iodine served as a catalyst, facilitating the oxidation of thiol groups to form disulphide bonds, which in turn resulted in the coupling of dithiol molecules into polymer chains. Post-reaction, iodine was removed during the work-up procedure.

A molar ratio of thiol groups to iodine was maintained at 2:1. Two polydisulphide products, corresponding to reaction times of 6 and 24 hours, were obtained and designated as DI06 and DI24, respectively. Thin-layer chromatography (TLC) analysis of 2,2'-(ethylenedioxy)diethanethiol showed a spot with an R_f value of 0.8. For DI24, the TLC revealed the disappearance of the initial reactant spot ($R_f=0.8$) and the emergence of a new spot ($R_f=0.4$), attributed to the product (Fig. 1).

The FT-IR spectra of dithiol, DI06, and DI24 (Fig. 2) demonstrated a vibrational absorption band at $2,556\text{ cm}^{-1}$ in the dithiol spectrum, attributed to the S-H stretch. This band was absent in the spectra of DI06 and DI24, likely due to the reduced intensity of the S-H vibrational signal in the longer polymer chains. Gel permeation chromatography (GPC) results indicated M_n and \bar{D} values of 13,100 and 1.15 for DI06, and 29,000 and 1.13 for DI24, respectively. These results reflect a step-growth polymerisation mechanism, wherein the coupling of thiol end groups forms disulphide bonds between repeating units. Longer reaction times resulted in higher conversion rates, yielding longer polymer chains.

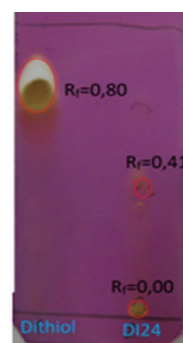


Fig. 1. Thin-layer chromatography results of 2,2'-(ethylenedioxy)diethanethiol and DI24.

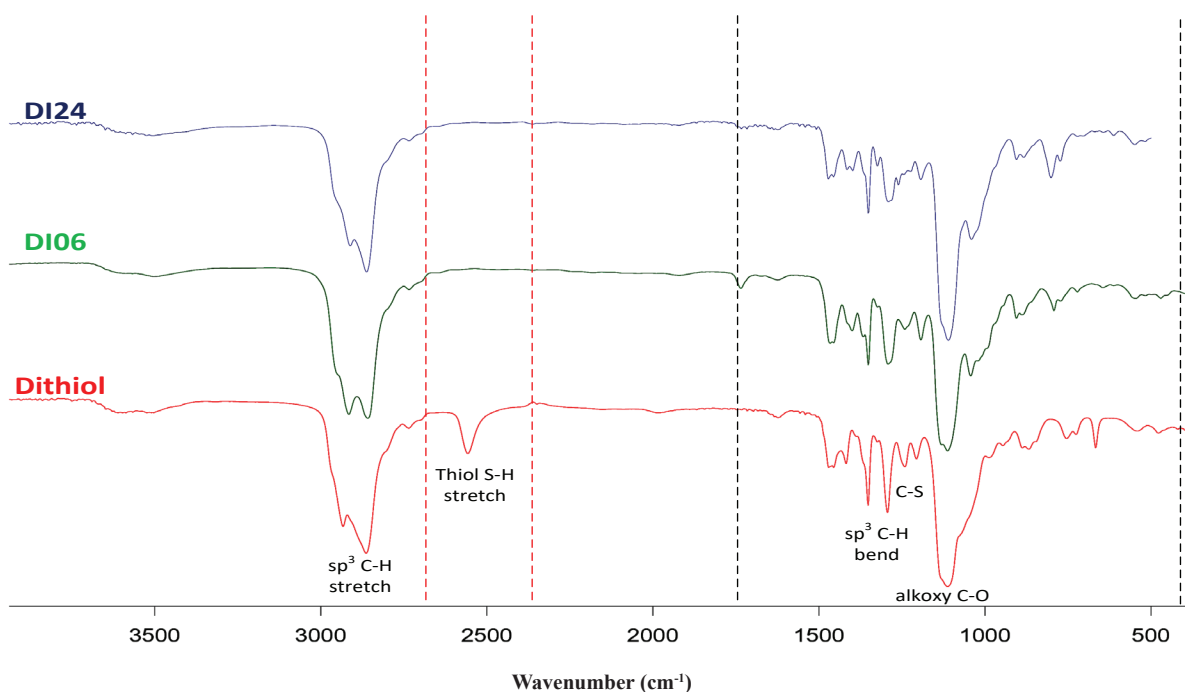


Fig. 2. Fourier transform infrared spectra of dithiol, DI06, and DI24.

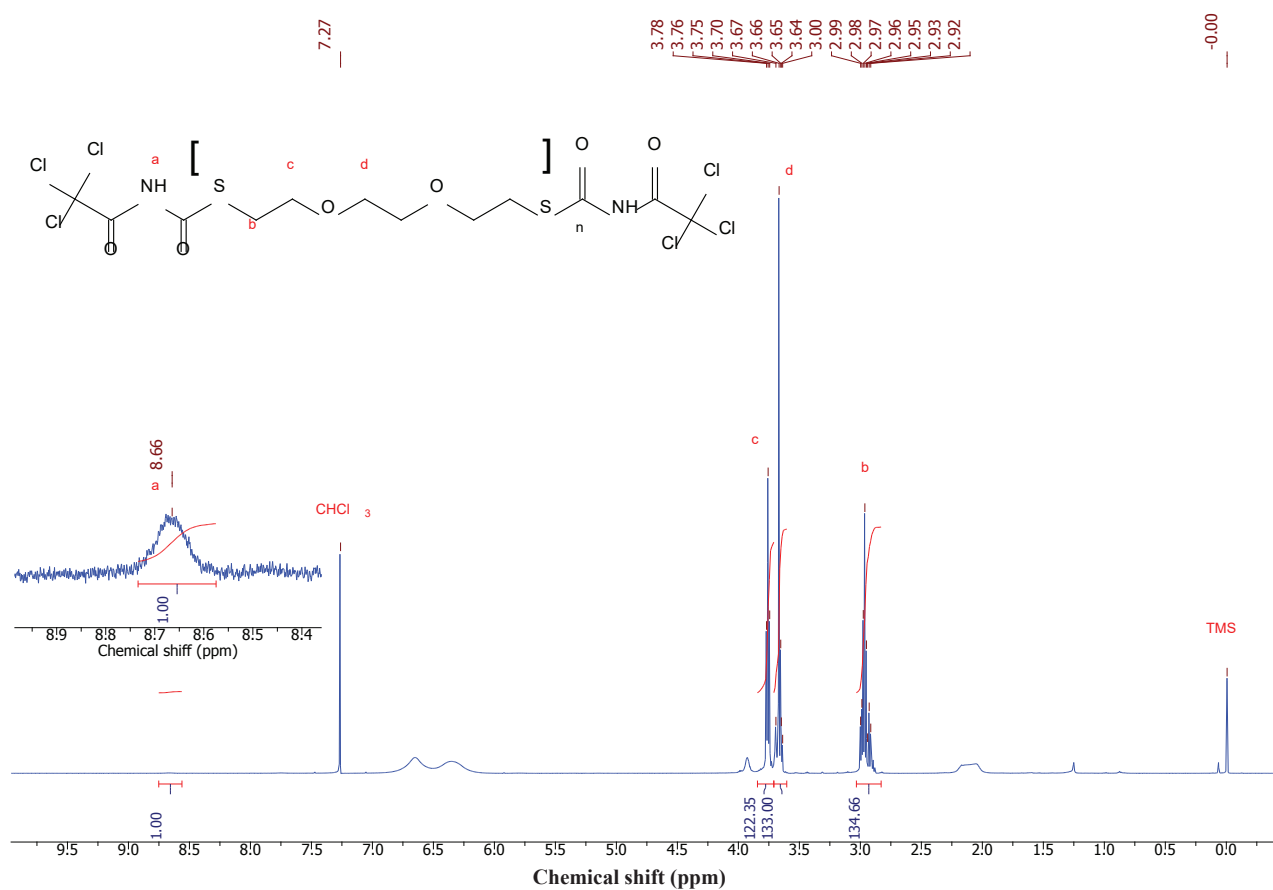
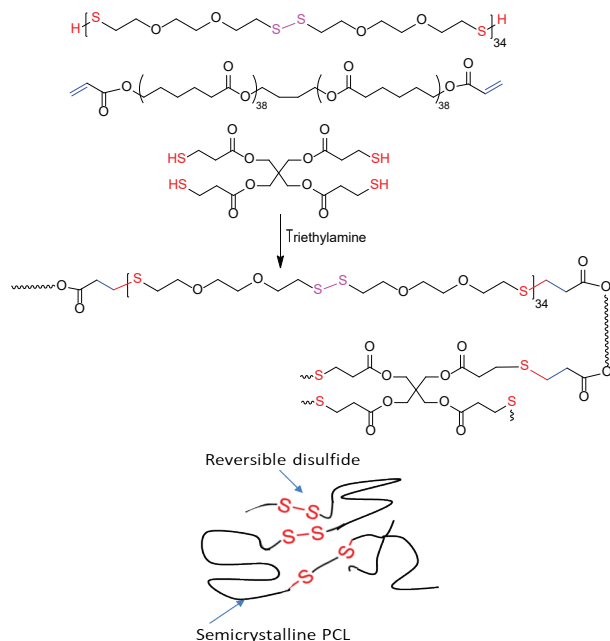


Fig. 3. Proton nuclear magnetic resonance spectrum of DI06 in the presence of trichloroacetylisocyanate.

^1H NMR analysis was further used to access the end groups of DI06 (Fig. 3). An excess amount of trichloroacetylisocyanate (TAI) reagent was mixed with the sample prior to analysis, according to the method for determining protic end-groups [14]. TAI reacts with thiol groups to form imidic groups ($-\text{S}-\text{C}(\text{O})-\text{NH}-\text{COCCL}_3$), with a signal at 8.66 ppm. The degree of polymerisation was estimated based on the integral ratio between the methylene proton signal and the imidic proton signal, yielding an M_n value of 12,214 g mol^{-1} .

3.2. Preparation of polydisulphide- and PCL-containing network

Next, polydisulphide DI06 was further mixed with tetrathiol and PCL-bisacrylate. Upon addition of triethylamine as a base catalyst, the thiol-acrylate Michael addition reaction occurred as a curing reaction (Scheme 2). The acrylate end groups of telechelically acrylate end-capped PCL reacted with both the thiol end groups of polydisulphide and the thiol groups of the tetrathiol-crosslinker via the thiol-acrylate Michael addition mechanism to form a network. An equimolar ratio between the acrylate and thiol groups was required to ideally obtain a network without any reactive thiol or acrylate groups left, while the molar ratio between tetrathiol and polydisulphide determined the crosslinking density of the network. A tetrathiol to polydisulphide molar ratio of 1:3 was chosen to produce a loosely crosslinked material.



Scheme 2. Synthesis scheme of disulphide- and polycaprolactone-containing network and a demonstration of the network.

Soxhlet extraction of the cured material yielded a gel fraction of $95\pm 2\%$. Comparison of FT-IR spectra (Figs. 4 and 5) for polydisulphide, tetrathiol, and the final network indicated the disappearance of absorption bands at 2556 cm^{-1} (S-H stretching) and 3080 cm^{-1} (C-H stretching in double bonds) in the network, confirming the complete reaction between acrylate and thiol groups.

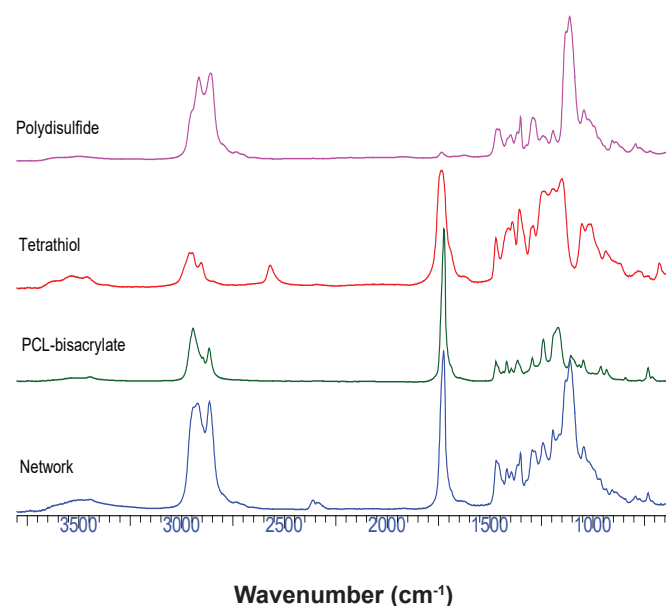


Fig. 4. Full Fourier transform infrared spectra of polydisulphide, tetrathiol, polycaprolactone-bisacrylate, and the network.

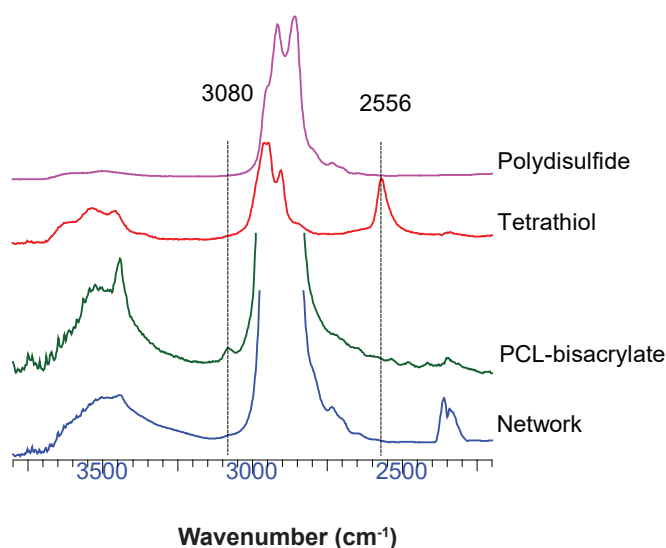


Fig. 5. Fourier transform infrared spectra in the region of $3,800\text{-}2,200\text{ cm}^{-1}$ of polydisulphide, tetrathiol, polycaprolactone-bisacrylate and the network.

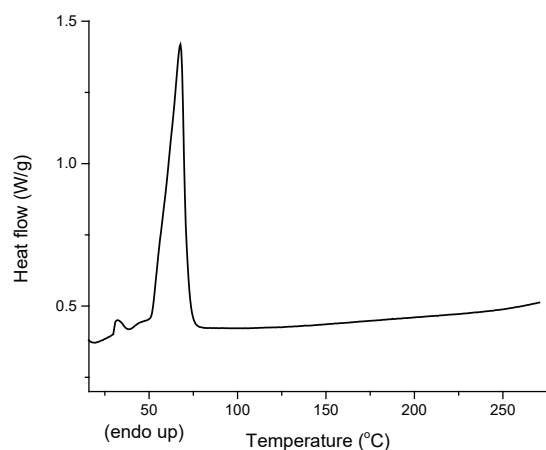


Fig. 6. Differential scanning calorimetry thermogram of the network.

The differential scanning calorimetry thermogram (Fig. 6) of the network showed an endothermic peak ascribed to the melting of the PCL crystalline phase at around 68°C.

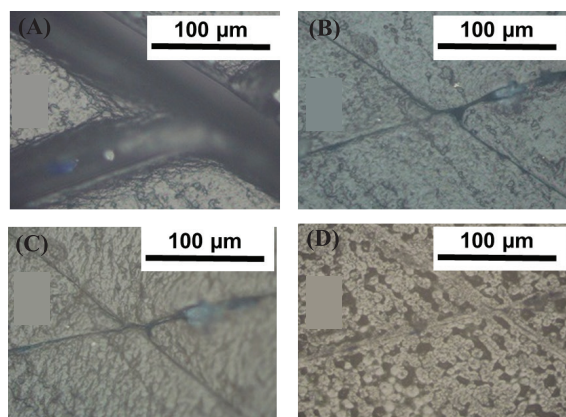


Fig. 7. Optical microscopic images of scratches on a network sample before healing (A) and after healing at 100°C for 1 hour (B), 6 hours (C), and 24 hours (D).

The resulting cast network sample after curing via the thiol-acrylate reaction exhibited an ability to heal scratches at 100°C. As shown from the optical microscopy result in Fig. 7, the scratches after being healed for 24 hours almost disappeared, indicating full healing. It should be noted that despite the network exhibiting shape-recovery at above 70°C (melting of the PCL crystalline phase), heating the scratch sample at a temperature range from 70 to 90°C only resulted in a small decrease in scratch width. Apparently, the healing behaviour at 100°C is attributed to the combined effect of PCL-induced shape recovery and the reversibility of disulphide bonds. Fig. 8 shows the stress-strain curves of

the network before healing and after healing at 100°C for 24 hours. A 62% recovery of the tensile strength was obtained after healing. A summary of the polydisulphide properties and the obtained network is given in Table 1.

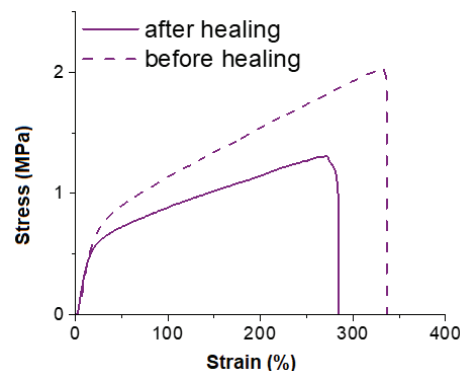


Fig. 8. Stress-strain curves of a network sample before healing (dashed line) and after healing at 100°C for 24 hours (solid line).

Table 1. Summary of the properties of polydisulphides and of the network.

Properties	Polydisulphide DI06	Polydisulphide DI24
M_n (GPC); D (GPC)	13,100 g mol ⁻¹ ; 1.15	29000; 1.13
M_n (¹ H NMR)	12,214 g mol ⁻¹	-
Gel content after crosslinking with PCL-bisacrylate	95%	-
Strength recovery after healing	62%	-
Ultimate strain recovery after healing	81%	-

4. Conclusions

In conclusion, a simple and efficient approach for the synthesis of polydisulphide- and polycaprolactone-containing networks with scratch mending ability has been successfully developed. A polydisulphide bearing thiol end groups with an M_n of approximately 12,000 g mol⁻¹ was obtained and further crosslinked with a PCL-bisacrylate and a tetrathiol-crosslinker to yield a network containing both semicrystalline PCL segments and disulphide linkages. The resulting material showed the ability of scratch healing.

CRedit author statement

Thuy Thu Truong: Methodology, Investigation, Writing - Original draft preparation; Le-Thu T. Nguyen: Conceptualisation, Supervision, Writing - Reviewing and Editing.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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