

Photoinduced Iron(III)-Mediated Atom Transfer Radical Polymerization with In Situ Generated Initiator: Mechanism and Kinetics Studies

Yin-Ning Zhou, Jun-Kang Guo, Jin-Jin Li, and Zheng-Hong Luo*

Department of Chemical Engineering, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

ABSTRACT: In this work, a photoinduced iron(III)-based atom transfer radical polymerization (ATRP) without any reducing agents and additional initiators was suggested. In addition, detailed kinetic studies, including the effects of ligand and catalyst concentrations on polymerization kinetics, and the polymerization behaviors using various solvents and monomer types were evaluated for this new polymerization technique. Results showed that photoinduced iron(III)-mediated ATRP using 5000 ppm catalyst loading with 1 equiv of ligand in *N*,*N*-dimethylformamide (DMF) produced poly(methyl methacrylate) with low molecular weight distribution ($M_w/M_n <$ 1.45) and that the evolution of molecular weight (M_n) was linearly related to monomer conversion. ¹H NMR analysis confirmed that the resulting polymer prepared through photoinduced ATRP in the present work was initiated by methyl 2,3-dichloroisobutyrate. Facile temporal control and the successful chain extension highlighted the good chain-end functionality of the resulting



polymers. In short, this work provided a study on additional alkyl halides initiator-free ATRP and its application in the synthesis of methacrylate polymers with narrow M_w/M_n .

INTRODUCTION

Atom transfer radical polymerization (ATRP) is one of the most robust reversible deactivation radical polymerization (RDRP) techniques, which is conducted by a reversible activation and deactivation equilibrium with transition-metal catalyst and alkyl halide.^{1–3} With the help of persistent radical effect, low concentration of radicals and suppressed side reactions enable polymerization to proceed in a controlled manner.⁴ Thereby, the preparation of well-defined polymers with versatile and precise architectures becomes accessible.^{2,3} Various transition metals, such as copper (Cu), iron (Fe), ruthenium (Ru), and nickel (Ni), coordinated by typical ligands were successfully employed in ATRP systems.^{5,6} Among them, iron complexes were considered to be an environment-friendly catalyst because of the low toxicity, low cost, and biocompatibility.^{7,8}

Initially, the Fe-based ATRP was reported by Sawamoto and co-workers and Matyjaszewski and co-workers in succession as early as 1997.^{9,10} Subsequently, a series of relevant studies toward iron-based ATRP were carried out using different iron complexes.^{11–17} However, high catalyst loadings and strict deoxygenization are required in conventional ATRP systems to maintain a favorable polymerization rate and controllability. In recent years, transition-metal complexes in a higher oxidation state or/and parts per million (ppm) catalyst loading was required in newly developed ATRP methods.^{2,3} These approaches can be divided into two types by the method of continuously regenerating activators: one is a chemical method

and the other is a physical method. As to the former, for example, the activators in reverse ATRP,¹⁸⁻²⁰ activators generated by electron transfer (AGET) ATRP, $^{21-27}$ activators regenerated by electron transfer (ARGET) ATRP,^{28,29} initiators for continuous activator regeneration (ICAR) ATRP, $^{30-37}$ and supplemental activators and reducing agent (SARA) ATRP³⁸⁻⁴¹ were continuously regenerated through using conventional radical initiator or organic-inorganic reducing agents. Besides, an Fe(III)-based ATRP using phosphorus ligands without any radical initiator [e.g., 2,2'-azobis-(isobutyronitrile) (AIBN)] and reducing agent was reported by Noh and co-workers, in which the authors proposed that the Fe(III) deactivator was reduced by methyl methacrylate at 80 °C.⁴²⁻⁴⁵ It should be noted that 2 equiv of phosphorus ligand was required for the catalyst coordination in these work. Nevertheless, an additional mechanism insight given by Matyjaszewski and co-wokers recently showed that phosphines play a dual role as reducing agents and ligand for Fe(III) salt in this system.^{17,46} Additionally, Noh and co-workers⁴⁷ and Bai and co-workers²⁰ reported a similar iron(III)-based polymerization system in the absence of any additional initiators (i.e., no radical initiator or alkyl halides initiator) under high

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temperature. However, different underlying mechanisms were proposed by these groups.

For the latter, the activators regenerated in polymerization system were achieved by using external physical stimuli, namely electrochemically mediated ATRP (eATRP)^{48,49} and photo-induced ATRP (photoATRP).^{50–69} Recent progress indicated that photoATRP is a powerful tool for the temporal and spatial control of polymerization.⁵⁰ For example, Hawker and coworkers explored a photoredox catalyst $[Ir(ppy)_3]$ and a metalfree ultraviolet light photoredox catalyst (10-phenylphenothiazine) for photoATRP.^{55,56} Interestingly, Miyake et al. realized energy-efficient polymerization methods, namely visible-light-induced ATRP, using organic visible-light photocatalysts (perylene and diaryl dihydrophenazines).^{57,4} Haddleton and co-workers studied the Cu(II)-mediated photo-ATRP from mechanism to application.⁶¹⁻⁶⁴ Aqueous photo-ATRP with ppm of Cu catalyst was also studied in Matyjaszewski's group.⁶⁷ More recently, Matyjaszewski and Jain and co-workers developed two Fe(III)-based photoinduced ATRP systems mediated by different catalytic complexes.^{68,6}

Different from previously reported works, this contribution suggested a photoinduced Fe(III)-mediated ATRP of methacrylate in the absence of any reducing agents and additional initiators. In this system, the reduction of the Fe(III) complex was induced by in situ ultraviolet (UV) light irradiation and mediated by methacrylate monomer. Subsequently, the resulting products of reduction reaction (i.e., alkyl 2,3dichloroisobutyrate and FeCl₂) initiated the polymerization. The proposed mechanism is illustrated in Scheme 1. The effects

Scheme 1. Proposed Mechanism of Photoinduced Iron(III)-Mediated ATRP in the Absence of Any Additional Initiator



of ligand and catalyst concentrations on the polymerization kinetics and the polymerization behaviors involving various solvents and monomer types were evaluated. The novelty of this as-developed polymerization system lies in giving further insight into the side reaction involved in conventional photoinduced Fe(III)-based ATRP using additional alkyl halides initiator on one hand and expanding the scope of photoinduced ATRP on the other.

EXPERIMENTAL SECTION

Materials. *tert*-Butyl methacrylate (tBMA, 99%, Sinopharm Chemical Reagent Co. (SCRC)) and methyl methacrylate (MMA, 99%, SCRC) were rinsed with an aqueous NaOH solution (5 wt %) to remove inhibitor, dried with MgSO₄ overnight, and distilled before use. 2-(Trimethylsilyl) ethyl methacrylate (HEMA-TMS) was prepared as in previous work.⁷⁰ Iron(III) chloride hexahydrate (FeCl₃·6H₂O, 99+%, Acros), iron(II) bromide (FeBr₂, 98%, Alfa), tris(4-methoxy-phenyl)phosphine (TMPP, 95%, Adamas). and *N*,*N*-dimethyl-formamide (DMF, 99.5%, TCI) were used as received. Acetonitrile (MeCN, 99.9%, Adamas) was continuously refluxed and distilled from CaH₂. Toluene (99%, SCRC) and anisole (99%, SCRC) were distilled from sodium before use.

General Procedure for Photoinduced Iron(III)-Mediated ATRP. Catalyst (FeCl₃·6H₂O, 38.3 mg, 0.142 mmol) and ligand (TMPP, 50.0 mg, 0.142 mmol) were first placed in a Schlenk flask with magnetic stirrer; then solvent (DMF, 3 mL) was added. Subsequently, the deoxygenated monomer (MMA, 3 mL, 28.3 mmol) was charged to the Schlenk flask, followed by three freeze-thaw-pump cycles. After that, the flask was put into a photochemical reactor equipped with an UV light. The photochemical reactor consists of a high-pressure mercury lamp equipped with an UV filter ranged from 300 to 400 nm $(\lambda_{\rm max} \sim 365 \text{ nm})$ and a circulating water cooling system. The reaction environmental temperature is 36 °C, and the intensity of the light source is $15 \pm 0.5 \text{ mW/cm}^2$. The reaction was stopped through exposure to air after a predetermined time. The solution was diluted with CHCl₃, filtered to remove the catalyst through passing through a basic alumina column, and precipitated in methanol. Samples were taken by syringe for kinetic analysis. Other polymerization systems involving different monomers and solvents were carried out following the same procedure.

General Procedure for Chain Extension Reaction under Conventional ATRP Conditions. A 192 mg sample of PMMA-Cl (19200 g/mol) synthesized via photoinduced iron(III)-mediated ATRP was charged into a flask with magnetic stirrer; then 1.5 mL of deoxygenated solvent (MeCN) was added. The solution containing a macroinitiator was transferred into a Schlenk flask charged with FeBr₂ (2.16 mg, 0.01 mmol) and TMPP (3.52 mg, 0.01 mmol). After three freeze-thaw-pump cycles, the deoxygenated monomer (MMA, 1.06 mL, 10 mmol) was injected to the Schlenk flask. The reaction mixture was immersed in an oil bath thermostated at 60 °C. The reaction was stopped through exposure to air after a predetermined time. The solution was diluted with CHCl₂, filtered to remove the catalyst through passing through a basic alumina column, and precipitated in methanol.

Characterization. Monomer conversion was monitored by proton nuclear magnetic resonance (¹H NMR) spectroscopy (Bruker AV400 MHz) in CDCl₃. Molecular weights and molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography (GPC, LC-20A, Shimadzu, Japan) using tetrahydrofuran as an eluent at a flow rate of 1.0 mL/min with a combination of two columns (Shodex, KF-802 and 804, 300 × 8 mm) and equipped with a RID-10A differential refractive index detector at 40 °C. A series of poly(methyl methacrylate) (PMMA) was used as the calibration standard.

RESULTS AND DISCUSSION

Kinetic Analysis of Photoinduced Iron(III)-Mediated ATRP. A series of photoinduced Fe(III)-based ATRP of methyl methacrylate (MMA) under different reaction conditions were carried out. As summarized in Table 1, it showed satisfactory results toward monomer conversion (about 40–60%) after

Table 1. Results of Photoinduced Iron(III)-Mediated $ATRP^{a}$

entry	$[M]_0:[C]_0:[L]_0$	time (h)	conv. (%)	$M_{ m n} \left({ m g/mol} ight) \left({ m GPC} ight)$	$rac{M_{ m w}/M_{ m n}}{ m (GPC)}$
1 ^b	200:1:1	10	0	N/A	N/A
2	200:1:0	10	47.4	15600	1.55
3	200:1:1	10	50.5	29000	1.45
4	200:1:1.5	10	55.6	17800	1.59
5	200:1:2	10	60.5	17700	1.63
6	200:0:1	10	40.5	87900	1.92
7	100:1:1	10	15.3	13800	1.30
8	100:0.2:0.2	10	56.1	36600	1.57
9	100:0.1:0.1	6	46.8	46200	1.87

^{*a*}Reaction conditions: monomer (M) = MMA; catalyst (C) = FeCl₃: 6H₂O; ligand (L) = TMPP; monomer = 3 mL; solvent = DMF; V_{monomer} : V_{solvent} = 1:1; light source = 15 mW/cm⁻² UV light (360 nm); temperature = 36 °C. ^{*b*}Without UV light irradiation.

reaction time of 10 h at near room temperature, except entries 1, 7, and 9. No polymer was obtained in entry 1 (Table 1), indicating that UV light irradiation is a necessary factor for triggering the polymerization.

Phosphines, such as triphenylphosphine (TPP), tris(2,4,6methoxyp- henyl)phosphine (TMPP), and tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP), are the most commonly used ligands in Fe-based polymerization systems.^{7,8} Previous works showed that higher reaction rate was observed by using electron-rich phosphines without losing control during the polymerization of MMA.^{13,17} In this work, TMPP with moderate activity was chosen. The result of entry 2 in Table 1 indicated that the polymerization was out of control in the absence of TMPP. When FeCl₃·6H₂O with 1 equiv of TMPP was used (Table 1, entry 3), the polymerization proceeded smoothly with efficient control. As shown in Figure 1A, an induction period was observed in each experiment, which is caused by the slow reduction of ${\rm Fe}^{\rm III}$ complex in solution system in responding to UV light. Figure 1B demonstrated that $M_{\rm n}$ increased linearly with monomer conversion (red data points), and low dispersity $(M_w/M_n < 1.5)$ was observed over the polymerization. The increase in TMPP concentration (Table 1, entries 4 and 5) resulted in the increase in polymerization rate with the value of M_w/M_n still around 1.5. However, the molecular weights did not increase with monomer conversion, which remained at about 17 000-18 000 g/mol. On one hand, excess TMPP would significantly

reduce $\text{Fe}^{\text{III}}\text{Cl}_3$ to $\text{Fe}^{\text{II}}\text{Cl}_2$, which caused the poor control and significant termination.¹⁷ On the other hand, phosphines can be also used as photoinitiator for MMA radical polymerization.⁷¹ A control experiment with only TMPP and no Fe(III) catalyst was carried out. The results are summarized in Table 1 entry 6; PMMA with $M_n = 87900$ g/mol and $M_w/M_n = 1.92$ was obtained after 10 h. This indicated that excess TMPP would induce polymerization under UV light irradiation, leading to the generation of new chains and also significant termination. These two aspects might thus give rise to the molecular weight with near-invariable value.

Table 1 (entries 3 and 7–9) and Figure 2 show the effect of catalyst loading on polymerization kinetics. Decreasing the catalyst loading from 10 000 to 1000 ppm (with respect to monomer) resulted in the increase in polymerization rate as demonstrated in Figure 2A. The linear semilogarithmic kinetic plot for 10 000 ppm catalyst concentration indicated that the concentration of radical species was low and constant. However, obviously curved semilogarithmic kinetic plots were observed for the polymerizations with 1000 and 2000 ppm catalyst loadings, indicating that significant radical terminations occurred. Figure 2B showed that faster polymerizations (1000 and 2000 ppm catalyst loadings) led to the formation of PMMA with higher molecular weights (>30 000 g/mol) and dispersities (>1.5). When 5000 ppm FeCl₃·6H₂O was used, monomer conversion reached ~50% after 10 h and $M_{\rm p}$ and $M_{\rm w}/M_{\rm n}$ of the resulting polymer were 29 000 g/mol and 1.45, respectively. The polymerization with 10 000 ppm FeCl₃·6H₂O smoothly proceeded to low conversion (\sim 15%) after 10 h, but PMMA formed with $M_{\rm p} = 13\,800$ g/mol and $M_{\rm w}/M_{\rm p} = 1.30$. The linearly increased molecular weight related to conversion allows one to control polymer molecular weight through the control of reaction time. As illustrated above, the catalyst loading could be reduced to 5000 ppm while still keeping a satisfactory monomer conversion after 10 h at such photoinduced iron(III)-mediated ATRP system without loss of controllability. These results demonstrated that the polymerization carried out with higher catalyst loading had a better control over M_n and its distribution. High deactivator concentration enabled the polymerization rate to slow, thus leading to efficient control. It should be pointed out that the production of the resulting polymers with both high molecular weight and low dispersity is a challenge in this system.

In addition to DMF, other solvents, i.e. MeCN, toluene, and anisole, were also used in photoinduced iron(III)-mediated



Figure 1. Effect of the ratio of ligand to catalyst on kinetics of photoinduced Fe(III)-based ATRP of MMA ([MMA]:[FeCl₃·6H₂O]:[TMPP] = 200:1:0/1/1.5/2): (A) semilogarithmic kinetic plot and (B) evolution of M_n and M_w/M_n with conversion.



Figure 2. Effect of the catalyst loading on kinetics of photoinduced Fe(III)-based ATRP of MMA ([MMA]:[FeCl₃·6H₂O]:[TMPP] = 100:0.1:0.1/ 100:0.2:0.2/200:1:1/100:1:1): (A) semilogarithmic kinetic plot and (B) evolution of M_p and M_w/M_p with conversion.

Table 2. Results of Photoinduced Iron(III)-Mediated ATRP of Various Methacrylates^a

entry	$[M]_0:[C]_0:[L]_0$	monomer (M)	solvent	time (h)	conv. (%)	$M_{\rm n}$ (g/mol) (GPC)	$M_{\rm w}/M_{\rm n}~({ m GPC})$
1	200:1:1	MMA	MeCN	10	25.4	31 200	1.38
2	200:1:1	MMA	anisole	10	27.0	31 800	1.44
3	200:1:1	MMA	toluene	10	40.1	28 900	1.58
4	200:1:1	tBMA	DMF	10	42.9	57 200	1.49
5	200:1:1	HEMA-TMS	DMF	10	56.7	85 200	1.70

^{*a*}Reaction conditions: $[M]_0: [C]_0: [L]_0 = 200:1:1$; monomer =3 mL; solvent =3 mL; light source =15 mW/cm⁻² UV light (360 nm); temperature =36 °C.



Figure 3. Kinetics of photoinduced Fe(III)-based ATRP of MMA with "on–off" light switch ([MMA]:[FeCl₃·6H₂O]:[TMPP] = 200:1:1): (A) semilogarithmic kinetic plot and (B) evolution of M_n and M_w/M_n with conversion.

ATRP of MMA under similar reaction conditions (Table 2, entries 1-3). With MeCN as solvent, monomer conversion reached ~25% after 10 h, yielding PMMA with $M_{\rm n}$ = 31200 g/ mol and $M_w/M_n = 1.38$. When using anisole as solvent, conversion was 27%, $M_{\rm p}$ and $M_{\rm w}/M_{\rm p}$ of PMMA obtained after 10 h reaction were 31 800 g/mol and 1.44, respectively. Solvents containing either an amide or a cyano group were able to facilitate the dissolution and stabilization of FeBr₂ or FeBr₃ to catalyzed ATRP.^{15,68} However, a tawny flocculent precipitate appeared during the polymerization using FeCl₃·6H₂O. It was speculated that the heterogeneous polymerizations in both MeCN and anisole might lead to their lower monomer conversion. When toluene was used, the resulting polymer yielded in this system after the same time gave $M_{\rm n} = 28\ 900\ {\rm g}/$ mol and M_w/M_n = 1.58. In comparison to other solvents, toluene involved polymerization resulted in poorer controllability. It can be concluded that an appropriate solvent needs to meet both requirements of high catalyst activity and good

controllability; DMF is adequate in photoinduced iron(III)mediated ATRP, at least in this catalyst system.

Furthermore, photoinduced iron(III)-mediated ATRP of tBMA and HEMA-TMS were carried out near room temperature. It could be seen that satisfactory monomer conversions (>40%) (Table 2, entries 4 and 5) were reached after reaction time of 10 h, and the molecular weights of resulting polymers were 57 200 and 85 200 g/mol for PtBMA and PHEMA-TMS, respectively. However, the controllability of both polymerizations was poorer than that of the MMA system. In particular, the HEMA-TMS polymerization system provided a polymer with $M_w/M_n = 1.70$. These results demonstrated that the activity of alkyl 2,3-dichloroisobutyrate was influenced by alkyl substituent as previous work reported,⁷² thus providing different degrees of polymerization controllability.

Temporal Control of Photoinduced Iron(III)-Mediated ATRP. Figure 3A shows the semilogarithmic kinetic plot for the "on-off" temporal controlled polymerization. The polymer-



Figure 4. ¹H NMR spectra of macroinitiator PMMA-Cl prepared via photoinduced iron(III)-mediated ATRP in the absence of additional initiator. a, a', b, c, and d are attributed to the protons of different groups in PMMA-Cl. The inset is a zoomed-in spectrum (3.43–3.83 ppm) of peak a.

ization proceeded smoothly to reach ~17% conversion with UV light irradiation for 4 h. The removal of the light source resulted in nearly no conversion in 2 h. This phenomenon could be attributed to the fact that activator Fe^{II} was no longer generated by the photoreduction of Fe^{III} in the dark. However, re-exposure of the reaction tube to the UV light led to restart of polymerization, and the conversion further increased to 31% after 2 h. It can be seen that the polymerization rate was higher than that of the first stage of polymerization, which indicated that the first stage required a longer reduction period. By performing multiple on-off operations, higher conversion could be reached. The following reaction rate remained the same as that of previous reaction period, suggesting robust activation and deactivation of polymerization. Additionally, the evolution of $M_{\rm p}$ increased linearly with conversion without being affected by the interruption of light source, as seen in Figure 3B. Low dispersities of resulting polymer were confirmed by the value of M_w/M_p ranging from 1.3 to 1.4.

Chain Extension of PMMA-Cl Prepared via Photoinduced Iron(III)-Mediated ATRP. High chain-end group fidelity is an important feature of a successful ATRP. It allows for the polymer chain functionalization and effective preparation of block copolymer and other well-defined macromolecules.

A macroinitiator PMMA-Cl prepared via photoinduced iron(III)-mediated ATRP using 5000 ppm catalyst was analyzed by ¹H NMR. In Figure 4, peaks a, c, and d located at 3.60, 1.80–2.00, 0.80–1.00 ppm were attributed to the protons of methoxy ($-OCH_3$), methylene ($-CH_2-$), and methyl ($-CH_3$) groups in PMMA, respectively. As seen in the zoomed-in region of the spectruem (3.43–3.83 ppm), peak a' with chemical shift at 3.78 ppm was assigned to the protons of the $-OCH_3$ neighboring the PMMA chain end. The ratio of areas of peak a and peak a' indicated the polymerization degree of PMMA was about 190. The calculated M_n was about 19 200 g/mol, which is close to the result (20 700 g/mol) obtained by GPC measurement, as shown in Figure 5. In addition, a



Figure 5. GPC traces of macroinitiator PMMA-Cl and block copolymer PMMA-*b*-PMMA.

shoulder peak b of peak a located at 3.66 ppm was observed and assigned to the protons of methylene $(-CH_2Cl)$ at the PMMA chain front-end. This result further confirmed that the resulting polymer prepared through photoATRP in the present work was initiated by methyl 2,3-dichloroisobutyrate.

Because the photoinduced Fe(III)-based ATRP demonstrated in the current work was a self-initiation system, the chain extension of PMMA-Cl was carried out under conventional ATRP conditions to avoid the influence of newly appeared propagation chains. As shown in Figure 5, the GPC results indicated that the macroinitiator PMMA-Cl had a wellcontrolled molecular weight distribution with $M_w/M_n = 1.34$. After chain extension of PMMA-Cl with MMA under FeBr₂catalyzed ATRP conditions, the resulting PMMA with $M_n =$ 29 900 g/mol and $M_w/M_n = 1.31$ was obtained. The GPC trace of the chain-extended PMMA showed a clear movement to higher molecular weight. The unimodal and nearly symmetrical shape of curves suggested good initiation efficiency and high chain-end functionality of the macroinitiator prepared by iron(III)-mediated photoATRP.

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CONCLUSION

In summary, a photoinduced iron(III)-mediated ATRP with in situ generated initiator at near room temperature was developed and investigated. In this system, the polymerization was initiated by alkyl 2,3-dichloroisobutyrate and FeCl₂/TMPP generated from in situ UV light irradiation. Detailed kinetic studies showed the following: (1) Excess TMPP would induce polymerization under UV light irradiation, leading to the significant termination and generation of new chains and thus give rise to the molecular weight with near-invariable value. (2)Polymerization carried out with higher catalyst loading had a linearly increased manner for the evolution of M_n with conversion and a better control of its distribution. However, high deactivator concentration could slow the polymerization rate. (3) Compared to MeCN, anisole, and toluene, DMF met both requirements of high catalyst activity and good controllability and thus is the preferred choice for photoinduced Fe(III)-mediated ATRP of methacrylate, at least in this catalyst system. (4) Because of the underlying mechanism of asdeveloped photoinduced Fe(III)-based ATRP and the different activities of alkyl 2,3-dichloroisobutyrate with different alkyl substituents, polymerization controllability varied with the type of methacrylate monomer.

Furthermore, ¹H NMR analysis of the macroinitiator PMMA-Cl confirmed the mechanism of the as-developed photoATRP. The on-off temporal controlled polymerization and chain extension reaction suggested that the as-developed system was a versatile photocontrolled polymerization technique and that it can be used for the synthesis of methacrylate polymers with narrow M_w/M_n and good chainend functionality. However, expanding the monomer scope of this polymerization approach further and producing a polymer with high molecular weight and low dispersity still need to be done.

AUTHOR INFORMATION

Corresponding Author

*E-mail: luozh@sjtu.edu.cn. Tel.: +86-21-54745602. Fax: +86-21-54745602.

Notes

The authors declare no competing financial interest.

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