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**Effect of Macromonomer Chemical Structure on the Rate of Grafting-Through Ring Opening Metathesis Polymerization†**

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## ARTICLE

# Effect of Macromonomer Chemical Structure on the Rate of Grafting-Through Ring Opening Metathesis Polymerization†

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Ring opening metathesis polymerization (ROMP) of norbornenyl macromonomers (MM) has become a preferred method to synthesize bottlebrush (BB) polymers with perfect grafting density. Prior investigations had established that fast ROMP rates were necessary to synthesize clean BB polymers and that the chemical structure of the anchor group linking the MM polymeric chain and norbornene unit had the most influence on the rate of ROMP. While the order of fastest anchor groups was predicted to be a general trend across all MM chemistry, we observed that the fastest anchor group for a poly(propylene oxide) (PPO) MM is not the fastest for a poly(lactic acid) (PLA) MM. From our kinetic analysis, we showed that PLA MMs are faster with a methylene linker and that PPO MMs are faster with a dicarboximide linker. Interestingly, however, the fast rate of the dicarboximide PPO MM did not lead to the synthesis of a PPO BB polymer with lower dispersity. While the root cause for this MM chemistry sensitivity is still unclear, this study shows that despite being far from the reactive group of the norbornene unit, the chemical structure of MM polymeric chain influences the rate of ROMP beyond the anchor group chemistry.

## Introduction

Bottlebrush (BB) polymers are a class of branched macromolecules where every repeat unit of a linear backbone is functionalized with a polymeric side chain. The steric repulsion of these side chains imparts an extended conformation to the BB polymers, which in turn reduces chain entanglements. As a result of their unique architecture and physical behavior, BB polymers are a promising platform for several different applications, such as photonic crystals, tunable elastomers, and drug delivery carriers.<sup>1–4</sup>

While several synthetic methodologies to access BB polymers exist, the grafting-through of norbornenyl terminated macromonomers (MMs) via ring opening metathesis polymerization (ROMP) has become one of the preferred synthetic routes, due to its ability to create BB with perfect grafting density and its ease to access multiblock structures.<sup>5</sup> The synthesis of clean BB polymers via graft-through ROMP has been shown to require the use of MMs that exhibit a high rate of polymerization. In contrast, slow MMs reach lower degree of polymerizations (DPs) and induce more catalyst deactivation which lead to broader molecular weight distributions (MWDs) and possibly incomplete consumption of the MM.<sup>6</sup> This need for fast MM polymerization has motivated many researchers to conduct in-depth investigations of the parameters that affect

the ROMP rate of MMs.<sup>5</sup>

The stereochemistry of the norbornenyl group has been shown to play an important role in the rate of ROMP. Exo-norbornenes are systematically faster than their endo-counterparts.<sup>7,8</sup> In addition to simply having slower kinetics, some endo- monomers have also been shown to form a stronger chelate with the catalyst metal center that competes with monomer coordination.<sup>9–11</sup>

The molecular weight of the MMs has also been shown to have a negative impact on the rate of ROMP. Larger MMs have been reported to polymerize more slowly than smaller MMs.<sup>12</sup> This effect has been attributed to an increase in steric hindrance around the catalytic center during polymerization. This size effect appears to reach a plateau once a certain size is reached.<sup>13–15</sup>

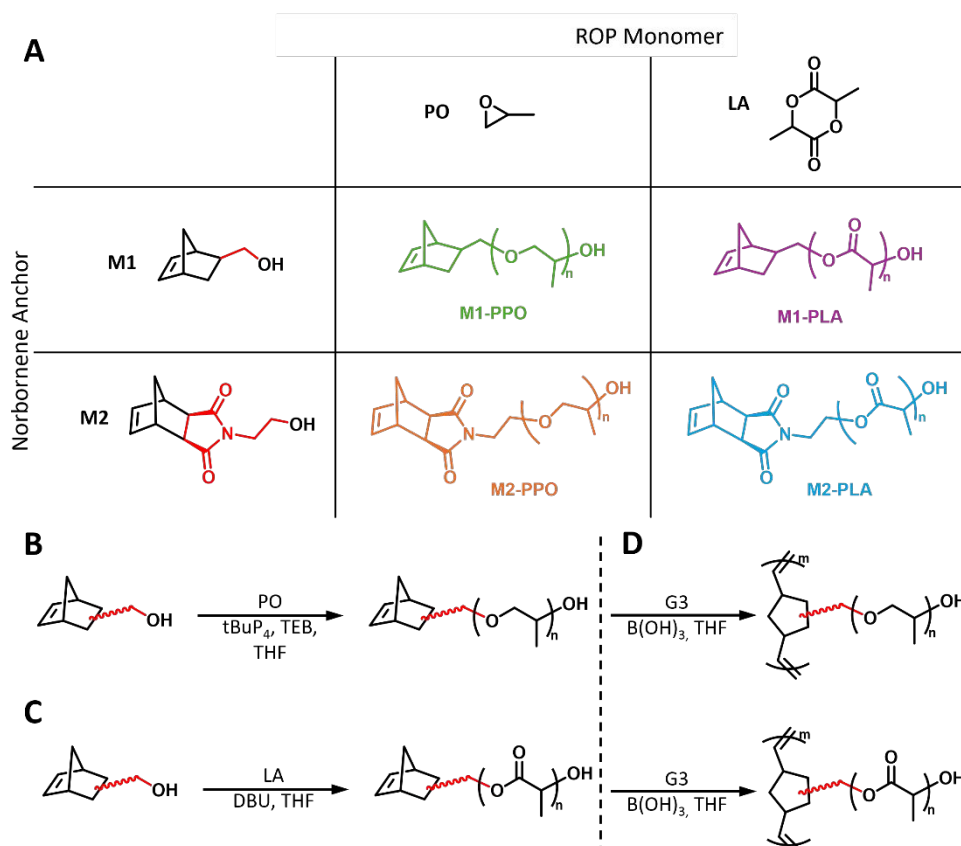
Finally, the effect of the chemical structure of the anchor group on the norbornene has also been shown to play a significant role in the rate of ROMP.<sup>16</sup> Dozens of anchor groups were diligently investigated to identify the fastest one.<sup>6,17,18</sup> The observed trend appeared to be agnostic of the polymer chemistry as no differences were observed between a poly(styrene) (PS) MM and a poly(lactic acid) (PLA) MM.<sup>6</sup> The difference in reactivity of these anchor groups was shown to be correlated to the HOMO/LUMO band gap of the norbornenyl unit.<sup>18</sup>

All these prior studies led to the conclusion that the chemical structure of the polymer chain attached to the anchor group does not affect the observed trends. This conclusion is supported by the fact that the polymer chain is more than seven

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**Fig. 1** (A) Norbornene anchors and ROP monomers used to synthesize the four MMs investigated in this study. General schemes for the synthesis of (B) PPO and (C) PLA MM followed by subsequent (D) ROMP in cascade.

carbons away from the reacting double bond in the norbornenyl unit.

Herein, we report a study where the MM polymeric chain structure appears to impact which norbornene anchor group is faster. More specifically, we confirmed previous work establishing that PLA MMs are faster with a methylene anchor group,<sup>6</sup> however, we found that poly(propylene oxide) (PPO) MMs are faster with a dicarboximide anchor group. Another contradiction that we observed is that the faster PPO MM does not yield the narrowest MWD polymer as it also causes faster degradation of the catalyst during the polymerization. While the root cause of this effect is part of an on-going investigation, our observations add a new aspect to consider while performing ROMP of norbornene-based MMs.

## Results and discussion

### Macromonomer Synthesis

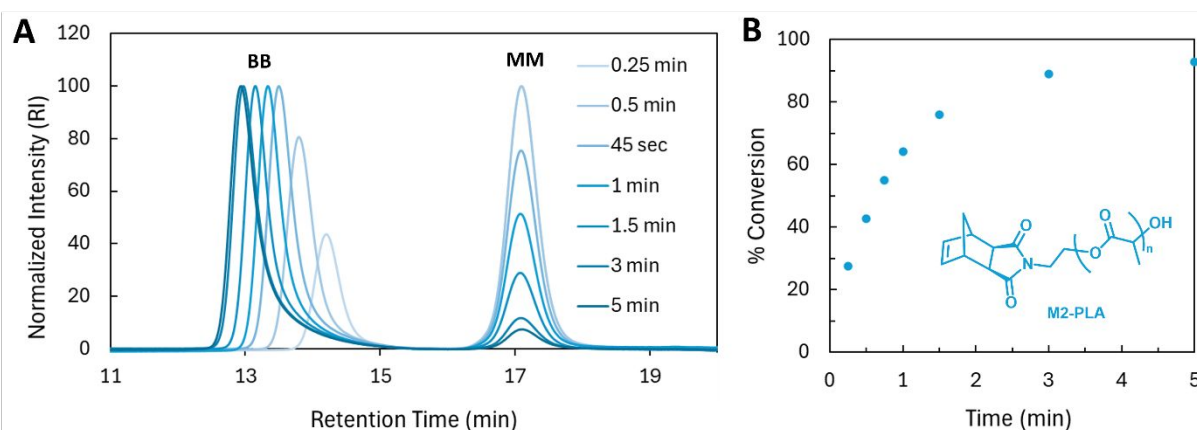
For this study, we examined the ROMP of four MMs comprised of two norbornenyl anchor groups, exo-5-norbornene-2-methanol (**M1**) and N-ethoxy-exo-5-norbornene-2,3-dicarboximide (**M2**), and two polymeric chains, PPO and PLA (Figure 1A). **M1** was previously established to be a faster anchor group compared to **M2**.<sup>6</sup>

All MMs were synthesized via ring opening polymerization (ROP) in THF using either **M1** or **M2** as alcohol initiators. The ROP of propylene oxide (PO) was conducted using a Lewis

acid/base pair consisting of triethyl borane (TEB) and P-tertbutyl phosphazene base ( $t\text{BuP}_4$ ) (Figure 1B).<sup>19,20</sup> The polymerizations were performed to completion in a sealed vessel (to prevent the evaporation of PO) and the polymers were characterized via size exclusion chromatography (SEC). The refractive index (RI) SEC traces of the PPO MMs show that the polymers have low dispersities ( $\text{Đ} < 1.1$ ) (Table 1, Figures S5-S6<sup>†</sup>). The ROP of D,L-lactide (LA) was performed using the organobase 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and was quenched at a moderate monomer conversion to prevent transesterification and broadening of the MWD (Figure 1C).<sup>13</sup> RI traces from SEC also show that all the PLA MMs have low  $\text{Đ}$  ( $< 1.2$ ) (Table 1, Figures S7-S8<sup>†</sup>). All PO and LA polymerizations were quenched with 1 mL of boric acid solution in THF (10 mg/mL), and the corresponding MMs were used for ROMP immediately after quenching, with no isolation or storage period (Figure 1D). A comparison study was conducted for the PLA MMs to demonstrate that MM isolation through precipitation did not impact the trends of the polymerization rates (*vide-infra*).

### ROMP Kinetic Studies

To compare the direct effect that the MM has on the rates of ROMP, we designed comparable ROMP experiments. The concentration of the MMs was kept constant at 20 mM and the backbone DP was targeted at 200 by using a molar ratio of 200:1 of MM to Grubbs third-generation catalyst (G3).<sup>8,21</sup> Kinetics of



**Fig. 2** (A) RI SEC traces from the ROMP of M2-PLA MM. Over time, the MM peak decreases in intensity as the BB peak increases in intensity and shifts to the left as it increases in molecular weight. (B) Calculated conversion from the ROMP of M2-PLA MM found using the ratio of BB peak area to the total combined area of MM and BB.

the polymerizations were measured by collecting 100  $\mu\text{L}$  aliquots of the reaction mixture and injecting them into vials containing 1 mL of an ethyl vinyl ether solution in THF (70  $\mu\text{L}/\text{mL}$ ). The quenched aliquots were then analyzed by SEC, where the MM conversion was determined by comparing the integrations of the BB and MM peaks from the RI traces (Figure 2, Figures S13-S16<sup>†</sup>). The MM conversion is shown to reach a maximum level for each polymerization, which indicates that the ROMP of the MMs reached completion (despite residual amount of MM present in the SEC trace caused by some non-norbornene initiated polymer) (Figure 2, Figures S13-S16<sup>†</sup>).

**Table 1.** Characterization of MM and BB Polymers

MM	MM $M_n^c$ (kg/mol)	MM $\bar{D}^c$	BB $M_n^c$ (kg/mol)	BB $\bar{D}^c$	$k_{\text{obs}}^d$ ( $\text{min}^{-1}$ )	Mean $k_{\text{obs}}$ ( $\text{min}^{-1}$ )	RSD $k_{\text{obs}}^e$ ( $\text{min}^{-1}$ )
M1-PPO <sup>a</sup>	4.5	1.0	205	1.2	1.41	1.47(9)	0.06
	4.1	1.0	168	1.2	1.57		
	4.5	1.0	190	1.3	1.43		
M2-PPO <sup>a</sup>	4.5	1.0	196	1.4	2.19	2.4(2)	0.08
	3.8	1.0	162	1.4	2.59		
	4.0	1.1	164	1.5	2.35		
M1-PLA <sup>b</sup>	4.8	1.1	307	1.1	4.32	4.6(3)	0.07
			281	1.1	4.68		
			275	1.1	4.89		
M2-PLA <sup>b</sup>	5.3	1.1	304	1.3	1.04	1.10(7)	0.06
			272	1.2	1.17		
			299	1.3	1.09		

<sup>a</sup>Separate batches of MM were used for ROMP kinetic studies. <sup>b</sup>Single batch of MM were split and used for ROMP kinetic studies. <sup>c</sup>Determined from RI SEC traces, measured in THF, using PS calibration standards. <sup>d</sup>Apparent rate constants calculated from polymerization conversion determined from reaction aliquots measured by SEC. <sup>e</sup>Calculated from  $k_{\text{obs}}$  as the standard deviation over the mean.

To analyze the ROMP kinetics, the MM conversions were first normalized to 100% and then applied to a first order rate law (Figure 3).<sup>10,22</sup> To ensure that differences in the size of the PPO and PLA MMs did not impact the polymerization rates, we opted to use MMs with similar sizes in solution. For that purpose, we used a PS calibration for the SEC to determine the MMs molecular weights. For simplicity, we also used the PS calibration to determine the  $\bar{D}$  of the BB polymers since we had

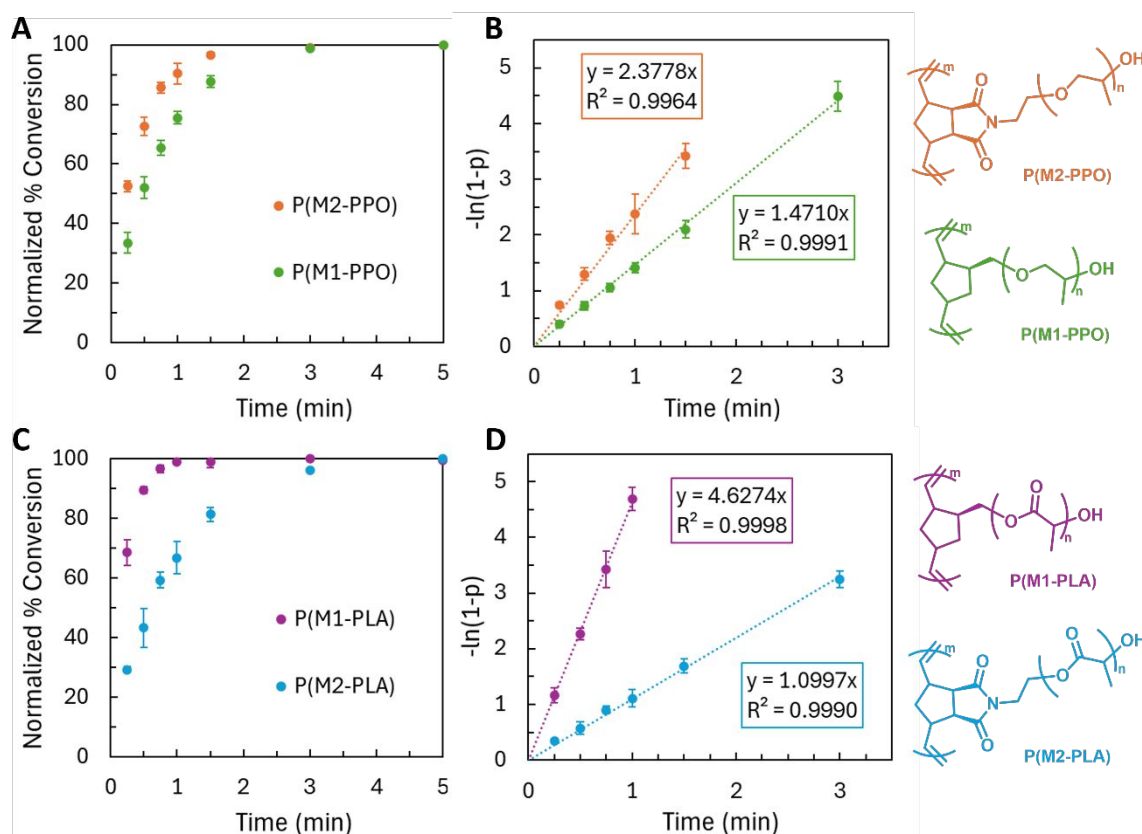
formerly established the validity of this methodology, especially when comparing values of chemically identical polymers.<sup>23</sup> We previously reported that at a number average molecular weight ( $M_n$ ) above 3.5 kg/mol, the impact of the molecular weight of **M1-PLA** MMs on the rate of ROMP becomes small,<sup>13</sup> and thus we targeted the  $M_n$ 's to be above 3.5 kg/mol for both PLA and PPO MMs (Table 1).

To further ensure that the rate of the PPO MMs would not be impacted by small batch to batch variances in  $M_n$ , three batches of **M1-PPO** and three batches of **M2-PPO** were individually synthesized (Table 1). While the PLA MMs were polymerized in triplicates, each of the six batches of the PPO MMs were polymerized once (Table 1). The apparent ROMP rates for each type of MM were then averaged, and the relative standard deviations (RSDs) of the averaged apparent ROMP rates were shown to be comparable (Table 1). This statistical analysis confirms that our rates of ROMP are not largely impacted by fluctuations of the  $M_n$  of the MMs.

As previously reported, the ROMP rate of **M1-PLA** was faster than the ROMP rate of **M2-PLA** ( $4.6 \pm 0.3$  vs.  $1.10 \pm 0.07$   $\text{min}^{-1}$  respectively, Table 1, Figure 3). Additionally, we saw a narrowing of the MWD in the resulting BB with the higher ROMP rates ( $\bar{D} = 1.1$  vs.  $1.2$  respectively, Table 1). The PPO MM ROMP rates go against both trends, with **M2-PPO** having a faster ROMP rate ( $2.4 \pm 0.2$  vs.  $1.47 \pm 0.09$   $\text{min}^{-1}$ ) and the resulting BB having a higher  $\bar{D}$  ( $1.4$  vs.  $1.2$ ) compared to **M1-PPO** (Table 1, Figure 3). The low molecular weight tail of the **M2-PPO** BB that causes the broadening of the MWD (and its asymmetry) seen in the SEC traces (Figures S10 and S14), is consistent with the deactivation of the growing polymer chain.<sup>8</sup> Despite the seven carbons separating the norbornenyl olefinic group and the polymer chain, the chemical structure of MM polymeric chain appears to influence both the rate of polymerization and the rate of catalyst deactivation.

### ROMP Control Experiments

We opted to not isolate the MMs before performing ROMP since precipitating low molecular weight polymers is tedious and results in loss of some polymer chains (fractionation of the MWD, see ESI, Section V<sup>†</sup>). Additionally, we have shown in the



**Fig. 3** Normalized % conversions for the ROMP of PPO MMs (A) and PLA MMs (C). Natural log plots calculated using normalized conversion, showcasing the ROMP rates observed for PPO MMs (B) and PLA MMs (D).

past that DBU, the catalyst for synthesizing the PLA MMs, becomes inert towards the ROMP initiator when quenched with boric acid and that boric acid itself has little effect on the rate of ROMP.<sup>13</sup> However, to confirm that the presence of the (quenched) ROP catalysts in solution were not the root cause for the trends we observed, we performed a series of experiments where we added the *other* ROP catalyst(s) before performing ROMP and compared the results to a control polymerization. In other words, we added DBU to the PPO MMs, and we added TEB and tBuP4 to the PLA MMs.

The loadings of the catalysts added corresponded to the loadings used for the respective MM syntheses (Table 2, Experiment 2). The  $M_n$ 's for each type of MM were once again kept above 3.5 kg/mol, allowing us to rule out any size effect and focus exclusively on the impact that the ROP catalysts have on the ROMP rate (Table 2). The trends observed previously, with PLA being faster with **M1** and PPO being faster with **M2** were maintained. For the PPO MMs, we observed a small decrease in the ROMP rates (1.70 to 1.65 min<sup>-1</sup> for **M1-PPO** and 2.46 to 2.23 min<sup>-1</sup> for **M2-PPO**, Table 2), which we expected since DBU becomes inert when exposed to boric acid, confirming that the presence of DBU did not impact the PLA MM ROMP rate trends. However, for the PLA MMs, we observed a 2-fold increase in the rates of ROMP after adding TEB and tBuP4 (5.60 to 10.12 min<sup>-1</sup> for **M1-PLA** and 1.81 to 3.66 min<sup>-1</sup> for **M2-PLA**, Table 2). We rationalize this increase due to TEB partly scavenging the bromopyridine bound to the G3 catalyst.<sup>24,25</sup>

Since the effect on the rate was the same for both PLA MMs, we concluded that TEB and tBuP4 also did not impact the trends we observed for the PPO MM ROMP rates.

**Table 2.** Characterization of MM and BB Polymers from ROMP Control Reactions

MM	Exp.	MM $M_n^c$ (kg/mol)	MM $\bar{D}^c$	BB $M_n^c$ (kg/mol)	BB $\bar{D}^c$	$k_{obs}^d$ (min <sup>-1</sup> )
M1-PPO	ctrl <sup>a</sup>	3.5	1.1	152	1.3	1.70
PPO	all <sup>b</sup>	3.7	1.1	143	1.3	1.65
M2-PPO	ctrl <sup>a</sup>	3.6	1.1	139	1.5	2.46
PPO	all <sup>b</sup>	3.5	1.0	135	1.5	2.23
M1-PLA	ctrl <sup>a</sup>	4.0	1.1	214	1.1	5.60
PLA	all <sup>b</sup>	4.0	1.1	197	1.2	10.12
M2-PLA	ctrl <sup>a</sup>	3.7	1.1	195	1.2	1.81
PLA	all <sup>b</sup>	3.8	1.1	185	1.3	3.66

<sup>a</sup>Control (ctrl) experiment where ROMP reaction only has ROP catalysts necessary for MM synthesis; TEB and tBuP4 for PPO; DBU for PLA. <sup>b</sup>Experiment where all ROP catalysts used for MM synthesis are added to the ROMP reaction; TEB, tBuP4, and DBU. <sup>c</sup>Determined from RI SEC traces, measured in THF, using PS calibration standards. <sup>d</sup>Calculated from polymerization conversion determined from reaction aliquots measured by SEC.

## Conclusions

We measured the ROMP rates of PLA and PPO MMs that have two different anchor groups and showed that the faster anchor group for the PLA polymers is the slower anchor group for the

PPO polymers, and vice versa. While we performed the graft-through polymerizations of the MMs without isolation, we demonstrated that the difference in the rate trends cannot be attributed to the different catalysts used to make the MMs. The trends for the PLA MM polymerization rates were the same as previously reported, with **M1** being the faster anchor group and yielding the lowest BB Đ. However, **M2** was measured to be the faster anchor group for the PPO MMs and surprisingly, this faster anchor group did not lead to a lower BB Đ compared to the slower anchor group for the PPO MMs (**M1**). While the root cause for this effect is not yet understood, and is the topic of ongoing consideration, this work empirically demonstrates that an anchor group optimization might be beneficial when synthesizing BB with different side chain chemistries.

## Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the ESI.†

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Dear Editor,

The data supporting this article have been included as part of the Supplementary Information.

Thank you,

A handwritten signature in black ink that reads 'Damien Guironnet' in a cursive script.

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