

## COMMUNICATION



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# Photocontrolled lactide ROP by the light-regulated release of potassium acetate from an azobenzene-bridged crown ether†

Quentin De Roover,<sup>ab</sup> Timothé Vucko,<sup>c</sup> Stéphane P. Vincent,<sup>id c</sup>  
Julien De Winter <sup>id b</sup> and Olivier Coulembier <sup>id \*a</sup>

An azobenzene-bridged 15-crown-5 ether (**1**) was successfully used as a photoswitchable cocatalyst for modulating the catalytic activity of potassium acetate (KOAc) in the ring-opening polymerization (ROP) of L-lactide (L-LA) when initiated from an exogenous alcohol. By alternating exposure to daylight and UV light, **1** transforms the K<sup>+</sup>, OAc<sup>-</sup> ion pair-like in free ions “on-demand”, resulting in an effective form of the catalytic complex. This allows the modulation of the L-LA ROP speed, switching the process from a slow to a fast state.

## Introduction

Modern polymer chemistry armed with controlled polymerization techniques and precision polymer functionalization allows materials scientists to produce an almost illimited choice of polymers on-demand. Despite various advances in the field, synthetic methods still pale in comparison to the nature. As an example, the synthesis of biopolymers, such as polypeptides, polynucleotides and polysaccharides, is known to be reversibly controlled by living systems, providing temporal and spatial control over those polymerizations.<sup>1</sup> Switchable catalytic polymerizations belong to a recent trend, which contribute to solving the grand challenges in materials science.<sup>2</sup> Among this rather young area of research, stimulus responsiveness provides a means of modulating both temporal and spatial domains.<sup>3</sup> Of the various stimuli employed to provide *in situ* control over the reversible activation of polymerizations, the use of light as a

regulative tool is advantageous due to its wavelength tunability, non-invasive character and precise operation in time and space.<sup>4</sup> Today, such ability to regulate catalyst activity is still underdeveloped, and reports on photoswitchable catalysts for ring-opening polymerization (ROP) processes are rare.<sup>5–14</sup> In ideal systems, the propagating polymer chain should switch between an “active” and a “dormant” state quickly. However, most of the current approaches are limited by using light to control only the initiation step or are characterized by the lack of repetitive cycles with high fatigue resistance.<sup>11</sup>

Recently, we have reported the use of crown ethers (CEs) to speed up the polymerization of L-lactide (L-LA) when initiated by an exogenous alcohol and catalyzed by potassium acetate (KOAc).<sup>15</sup> CEs played a crucial role as a KOAc complexing agent producing *in situ* free ions, well more appropriate to activate the propagating alcohol for the ring-opening reaction of L-LA. We reasoned that if the binding ability of the ion CE carrier can be changed by light, it would lead to a photocontrolled ROP process. Bis(CEs), which are able to adopt a face-to-face orientation, are known to exhibit higher binding abilities towards large metal cations than the corresponding mono(CEs).<sup>16–20</sup> Shinkai and Manabe demonstrated that photoresponsive bis(15-crown-5 ether) with an azobenzene linkage (**1**) efficiently acts as a phototweezer for the K<sup>+</sup> cation transport.<sup>20</sup> While *trans*-**1** is isomerized by UV light to *cis*-**1**, *cis*-**1** is easily isomerized to *trans*-**1** under visible light (or thermal treatment), the interconversion being reversible as the motion of a butterfly (Fig. 1).

<sup>a</sup> Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons, Place du Parc 23, 7000 Mons, Belgium. E-mail: olivier.coulembier@umons.ac.be

<sup>b</sup> Organic Synthesis and Mass Spectrometry Laboratory (S2MOs), Materials Institute, University of Mons, Place du Parc 23, 7000 Mons, Belgium

<sup>c</sup> Unité de Chimie Organique, Université de Namur ASBL, Rue de Bruxelles 61, 5000 Namur, Belgium

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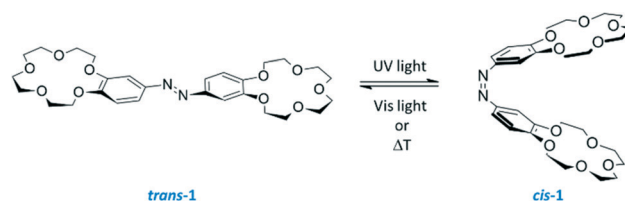


Fig. 1 Butterfly-like motion of the **1** cocatalyst.

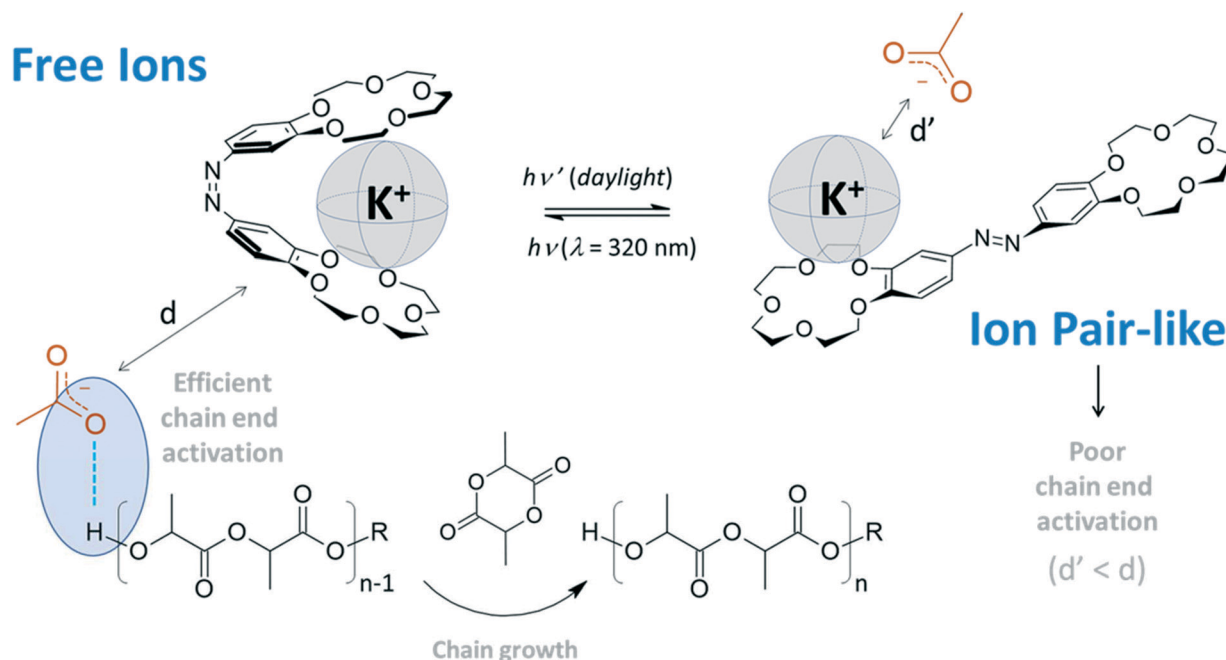


Fig. 2 Photocontrol over L-lactide polymerization using a KOAc/1 complex.

Herein, we present the first catalytic complex for which the reactivity is controlled by the reversible transformation of  $K^+$ , $^-OAc$  ion pair to reactive free ions through the photoisomerization of cocatalyst **1** (Fig. 2).

## Results and discussion

Prior to investigating the photocontrolled ROP of L-LA, photocatalyst **1** was prepared in a two-step process from the commercially available 4-nitrobenzo-15-crown-5. After reduction in 4-aminobenzo-15-crown-5, the primary aromatic amine was treated by the heterogeneous use of potassium permanganate supported on copper(II) sulfate pentahydrate, leading to azobenzene-bridged 15-crown-5 (**1**).<sup>21</sup>

The light-triggered isomerization of azobenzene-based compounds presents some interesting features, including non-demanding reaction conditions at the exception of the use of a UV-vis alternating lamp-equipped chamber that could limit the applicability of such a strategy to privileged research groups in the world. This motivated us to develop simpler alternatives to the experimental device concerned. In particular, we considered other visible light emission sources, which in turn would be available without any special equipment. Therefore, in the present contribution, we took advantage of the free natural visible radiation from the sun, *i.e.* a daylight (DL) treatment, instead of a specific visible light source.

To account for the effect of the  $K^+$  cation on the photoisomerization of **1** and perfectly mimic the next polymerization conditions, the *E*-to-*Z* isomers ratio was determined by <sup>1</sup>H-NMR in the presence of one equivalent of the KOAc catalyst in a  $[D_8]THF$  solution. While pristine **1** presents an *E*-to-*Z* ratio of 97/3 under daylight at 21 °C, the

addition of 1 eq. of KOAc affects the relative concentration of the *cis*-1 isomer, leading to an *E*/*Z* ratio of 81/19. The increase in the *Z*-form is due to the “tying” effect of the  $K^+$  cation.<sup>20</sup> Irradiation of the solution with light at the wavelength of 320

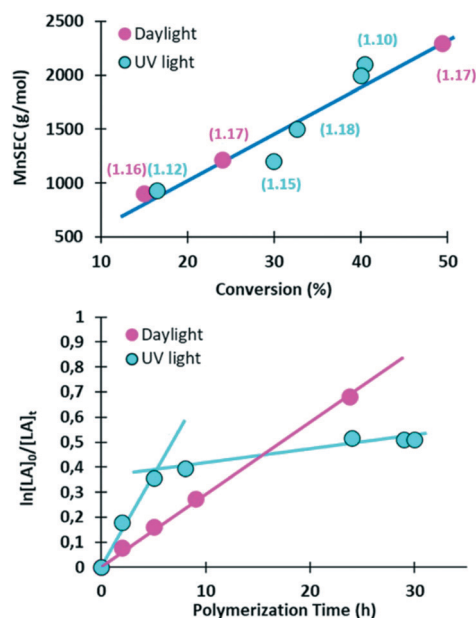
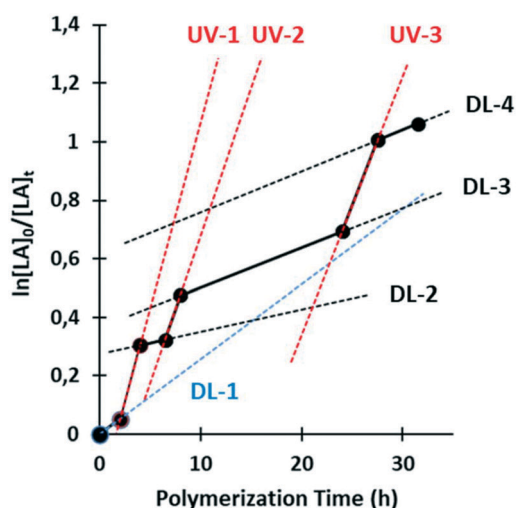
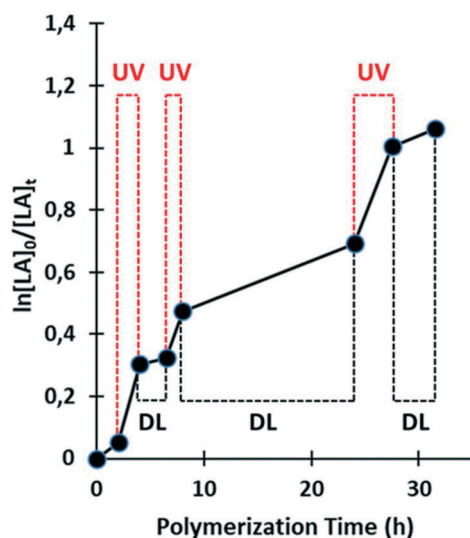


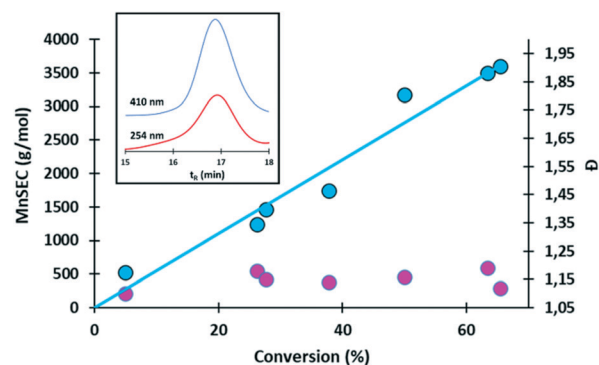
Fig. 3 Top. SEC experimental  $M_n$  in function of the conversions recorded during the L-LA polymerizations initiated with BnOH and catalysed with  $[KOAc]_0/[1]_0 = 1$  in THF under daylight (●) and UV light (●). Dispersity values are under brackets; Bottom. Semilogarithmic plots of L-LA polymerizations initiated with BnOH and catalysed with  $[KOAc]_0/[1]_0 = 1$  in THF under daylight (●) and UV light (●). Conditions of polymerizations:  $[L-LA]_0/[BnOH]_0/[KOAc]_0/[1]_0 = 40/1/0.5/0.5$ ,  $[L-LA]_0 = 1$  M, 21 °C.



**Fig. 4** Semilogarithmic plot of *L*-LA polymerizations initiated with BnOH and catalysed with  $[\text{KOAc}]_0/[\mathbf{1}]_0 = 1$  in THF with alternation of DL and UV light. Conditions of polymerizations:  $[\text{L-LA}]_0/[\text{BnOH}]_0/[\text{KOAc}]_0/[\mathbf{1}]_0 = 40/1/0.5/0.5$ ,  $[\text{L-LA}]_0 = 1 \text{ M}$ , 21–23 °C. Top. Visualization of the type of light applied. Bottom. Visualization of the ROP rate variation symbolized by the dash lines: red = UV treatment, black = UV lamp off during the daylight propagation, blue = daylight treatment during the initiation step.

nm led to photoisomerization to yield an *E/Z* ratio of 53/47, after 2 h. The non-quantitative formation of the *cis*-1 isomer is explained by reaching a photo stationary state (PSS) not only due to a small absorbance of *Z*-isomers but also a thermal sensitivity of **1** under the experimental set-up conditions. This has been clearly observed by irradiation of the solution under UV light for 17 h. After such a long time of irradiation, the temperature of the medium increases to ~40 °C diminishing the *cis*-isomer proportion to 40%.

With the photoswitchable cocatalyst **1** in hand, the catalytic activity of the KOAc/**1** complex in the ROP of *L*-LA was then studied (Fig. 2). The polymerization conditions already established by us for non-switchable KOAc/crown ethers<sup>15</sup> were used. Polymerizations were then conducted in



**Fig. 5** Evolution of  $M_{n\text{SEC}}$  (●) and  $\bar{D}$  (●) versus conversion recorded during the *L*-LA polymerizations initiated with BnOH and catalysed with  $[\text{KOAc}]_0/[\mathbf{1}]_0 = 1$  in THF with alternation of DL and UV light (see Fig. 4). Inset: SEC traces of the PLA sample obtained after 31.5 h using both RI (410 nm) and UV (254 nm) detectors.

dry THF containing *L*-LA in a concentration of 1 M and monitored by the size-exclusion chromatography (SEC) analysis. Instead of the commonly used pyrene-based initiator for enhanced ultraviolet light detection in SEC measurements of the final polymer,<sup>22–24</sup> benzyl alcohol (BnOH) was used as initiator to not interfere with the 320 nm ultraviolet light-triggered photoisomerization process. Polymerizations were then performed at 21 °C for a  $[\text{L-LA}]_0/[\text{BnOH}]_0/[\text{KOAc}]_0/[\mathbf{1}]_0$  of 40/1/0.5/0.5. Under daylight, the kinetic plot gave a straight line in the semilogarithmic coordinates attesting that the number of growing chains does not change appreciably during the ROP, at least till 50% conversion (Fig. 3, bottom). Interestingly the isomer *trans*-1 appears as a mediocre but in a sense effective cocatalyst to polymerize *L*-LA by complexing the KOAc as a poorly active ion pair-like structure. Under UV light, the polymerization is initially faster but levels off after ~5 h of reaction. Initially ascribed to a loss of control during the UV-triggered ROP process, such hypothesis was refuted by the linear evolution of  $M_{n\text{SEC}}$  vs. conversion and the narrow dispersities ( $\bar{D} = M_w/M_n$ ) recorded whatever the applied DL or UV light treatment (Fig. 3, top). The end-group fidelity was also confirmed by the MALDI-ToF analysis (see ESI†).

A possible explanation could come from the increase of the temperature during the UV light exposure. As experimentally recorded, the temperature changed significantly, increasing from 21 °C to almost 35–40 °C after 5 h. Such increase in temperature drastically shifts the *cis*-to-*trans* equilibrium to the less active *trans*-1 isomer and is also unfavourable for the  $\text{K}^+$  cation–crown ether complexation.<sup>25</sup> To get rid of this negative thermal effects, UV irradiation periods were limited to 4 h maximum. Fig. 4 demonstrates clearly that the polymerization of *L*-LA can be switched between slow and fast states by alternating exposure to UV light and daylight.

Analysis of the polymer after three successive UV/DL cycles (~31.5 h) revealed a 66% conversion of the monomer to afford polylactide with a  $M_n$  of 3600  $\text{g mol}^{-1}$  ( $\bar{D} = 1.12$ ), in

**Table 1** Approximation of the apparent rate constants calculated during the UV/DL treatments<sup>a</sup>

Step	Apparent rate ( $10^{-2} \text{ h}^{-1}$ )	Illumination time (h)	Conversion window (%)
DL-1	2.6	2	0–5
UV-1	12.6	2	5–26.2
DL-2	0.8	2.5	26.2–27.6
UV-2	10.1	1.5	27.6–37.8
DL-3	1.4	16	37.8–50
UV-3	8.9	3.5	50–63.4
DL-4	1.4	4	63.4–65.4

<sup>a</sup> See Fig. 4 caption for experimental conditions.

perfect agreement with the theoretical  $M_n$  of  $3800 \text{ g mol}^{-1}$ . A plot of the molecular weight ( $M_{n,SEC}$ ) and the dispersity value *versus* conversion was linear and the SEC traces for the polylactide using both refractive index and UV detectors (410 nm and 254 nm, respectively) clearly show a quantitative and statistical distribution of the phenyl group in the sample, confirming the effective initiation from BnOH (Fig. 5). Fig. 4 (bottom) helps to compare the semilogarithmic plot slopes of each illuminating treatment by the juxtaposition of extended dash lines. Red-dashed lines help to compare slopes (and the reaction rates) between each UV treatments, while black-dashed lines symbolize the slopes during DL treatments.

As illustrated, whatever the illumination cycle, polymerization rates observed during both DL and UV light exposures are roughly identical (see the approximated rate values in Table 1). On average, the rate of polymerization during the UV treatment is  $\sim 9$  times higher than the one recorded during the DL treatment. This confirms the ability of the cocatalyst **1** to control the equilibrium between  $K^+$ ,  $^-OAc$  ion pair and free ions and to modify on-demand the L-LA ROP kinetics under appropriate illumination. In contrast, the reaction rate observed during the first steps of the polymerization (symbolized by the blue dash line) is elevated. Such an effect (here limited to a conversion of 5%,  $DP_{th} = 2$ ) is associated to the polymerization mechanism consisting here in a basic chain end activation from the acetate ion catalyst (Fig. 2).<sup>15,26</sup> However, during the propagation, acetate has to activate a lactidyl secondary alcohol, and the initiation consists of activating BnOH. Since the primary alcohol of BnOH is more nucleophilic and acidic than the lactidyl one, this explains the kinetic boost observed for such low conversion.

## Conclusions

In summary, we have successfully developed a concept to control the catalytic activity of the KOAc/**1** complex by a light-induced treatment. Our experiments confirm the ability of the cocatalyst **1** to control the equilibrium between  $K^+$ ,  $^-OAc$  ion pair and free ions on-demand to modify the L-LA ROP kinetics under appropriate illumination. This allowed the modulation of the polymerization speed, switching the process from a slow to a fast state ( $k_{fast}/k_{slow} \sim 10$ ) for

multiple cycles. In the light of simplicity, we also report that the daylight-induced isomerization may be employed rather than specific visible radiation, avoiding a complex experimental set-up. The alteration of the catalytic activity described here should allow for the light-regulated construction of polymers with controlled chain structures.

## Author contributions

O. C. conceived the project and designed the experiments. Q. De R. performed majority of the experiments and data analysis. T. V. and S. P. V. supervised the synthesis of **1**. The manuscript was written by O. C. and edited by all the co-authors.

## Conflicts of interest

There are no conflicts to declare.

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