

# Dimerization of Methyl Acrylate through CO<sub>2</sub>-pressurized DBU Mediated Process

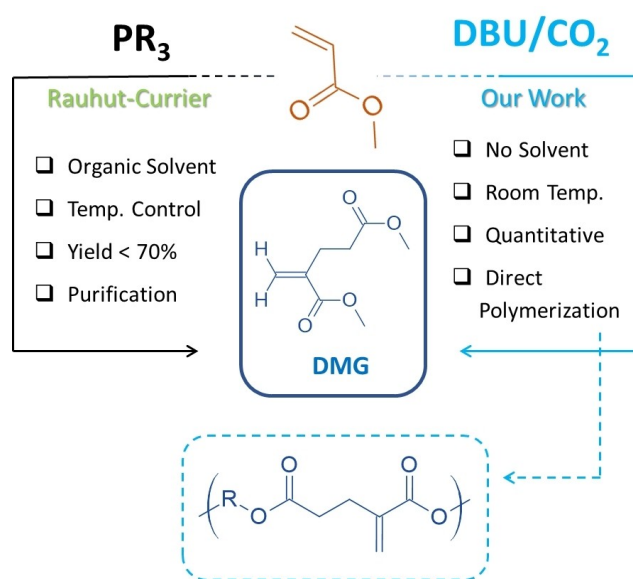
Sébastien Moins and Olivier Coulembier\*<sup>[a]</sup>

**Abstract:** A selective and facile methyl acrylate (MA) head-to-tail dimerization process is here presented. The dimerization is articulated on the use of the 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) amidine organic base and the carbon dioxide (CO<sub>2</sub>) working gas used as mediator and water trap, respectively. Under moderated pressure of CO<sub>2</sub> (20 to 40 bars), the selective production of MA dimer is carried out

in bulk condition and at room temperature, offering perspectives to an industrially scalable process. The purity of the non-isolated dimer is such that it could be directly step-growth copolymerized with a diol taking profit of the presence of the amidine organic base acting as transesterification agent.

Methyl acrylate (MA) is one of the most important and readily available polar vinyl monomers. Easily made from very cheap raw materials and produced on a vast industrial scale, the use of such inexpensive acrylic compound as starting substrate in organic synthesis is of particular interest. Today plethora of synthetic methods used in converting MA in usable products, including polymers, have been reported<sup>[1–7]</sup> but data on its dimerization are rare.<sup>[8–12]</sup> The head-to-tail MA dimer, *i.e.* dimethyl  $\alpha$ -methylene-glutarate (DMG, Figure 1), is the smallest representative of saturated branched MA dimers. Already studied for its radical polymerization ability,<sup>[13–15]</sup> DMG offers interest and new perspectives in material science in the same way as the 2-ethylidene-3-methylpentanedioates recently prepared by dimerization of crotonates providing a sustainable route to difunctional monomers for step-growth polymerizations.<sup>[16]</sup>

Although various aliphatic phosphine catalysts such as tri(*n*-butyl)phosphine have been reported for the DMG synthesis, they generally afford non-quantitative yields (~50–70%) requiring a DMG purification by distillation.<sup>[8]</sup> The highly exothermic dimerization of MA necessities to be thermally controlled and is carried out in organic solvents such as acetonitrile or dioxane. According to the initial experimental data reported by Rauhut and Currier,<sup>[8]</sup> the process needs also to be performed under anhydrous conditions since final DMG yield decreases as the amount of water present increases. Accordingly, the Rauhut-Currier reaction, even if of indisputable interest, could not be foreseen as industrially scalable. Herein, we report a facile and selective MA dimerization process articulated on the use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as mediator and carbon dioxide (CO<sub>2</sub>) as a water trap (Figure 1). In order to meet basic industrial constraints, all reactions were performed with prod-



**Figure 1.** Synthesis characteristics adopted during both the Rauhut-Currier and our proposed reactions for the production of dimethyl  $\alpha$ -methylene-glutarate (DMG) from methyl acrylate.

ucts as-received. Vessels and DBU were undried and MA still contained its stabilizer.

According to reported data,<sup>[11,17,18]</sup> 1,4-diazabicyclo[2.2.2]octane (DABCO) is an efficient catalyst for the Baylis-Hillman reaction but is unactive for the dimerization of methyl acrylate in a Rauhut-Currier process. Interestingly, Aggarwal and Mereu demonstrated that DBU is actually the optimum organic catalyst for the Baylis-Hillman reaction, providing adducts at much faster rates than using DABCO.<sup>[19]</sup> Reasoning that both Baylis-Hillman and Rauhut-Currier reactions proceed by formation of an initial Michael adduct, we though interesting to investigate the effect of DBU as a Rauhut-Currier mediator for the dimerization of MA.

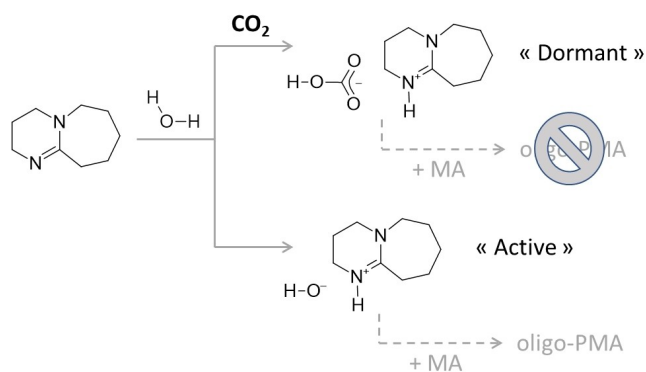
First investigations were made at r.t. under the air for an initial [MA]<sub>0</sub>/[DBU]<sub>0</sub> ratio of 1. As observed by both <sup>1</sup>H-NMR and SEC techniques, after 24 hours, less than 10% of MA was

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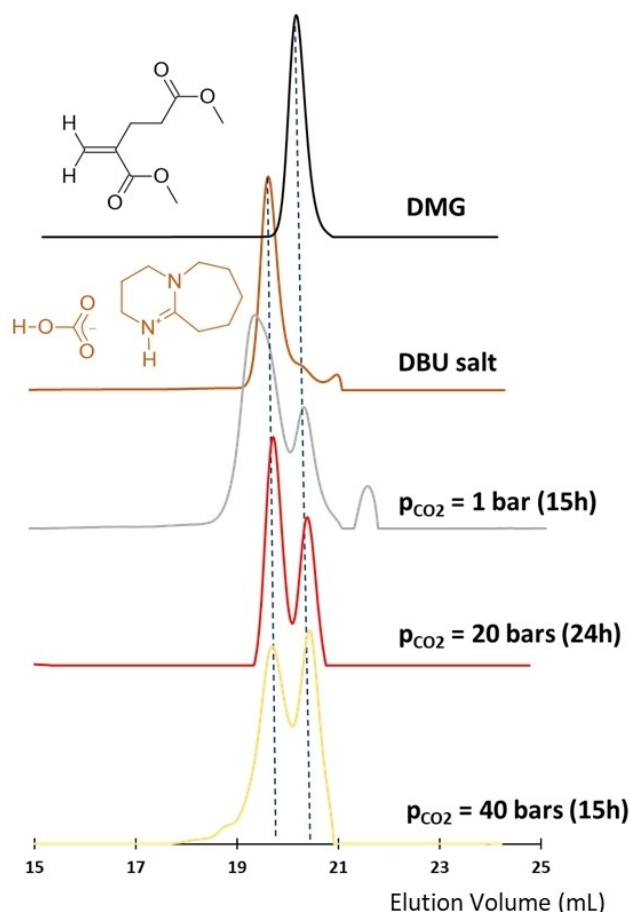
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converted in oligo-poly(methyl acrylate) (oligo-PMA) of number-average molar masses ( $M_n$ ) of around 2000  $\text{g}\cdot\text{mol}^{-1}$ . While same conclusions were drawn for an initial  $[\text{MA}]_0$ -to- $[\text{DBU}]_0$  ratio of 10, increasing the reaction time to 7 days does not have any effect on the MA dimerization selectivity. To our own opinion, the uncontrolled formation of oligo-PMA is attributed to the presence of residual water. While pristine DBU is known to poorly catalyze the anionic polymerization of MA from a  $-\text{CH}^{(-)}\text{R}$  propagating group,<sup>[20]</sup> it also easily reacts with water to form a  $\text{HO}^{(-)}$ ,  $\text{DBU}\cdot\text{H}^{(+)}$  ionic species. Since alkoxide structures, such as  $\text{RO}^{(-)}$ ,  $\text{X}^{(+)}$  are known to conduct the anionic oligomerization of MA,<sup>[21]</sup> it is reasonable to believe that oligo-PMA are here produced from *in situ* generated  $\text{HO}^{(-)}$ ,  $\text{DBU}\cdot\text{H}^{(+)}$  initiating species. Studies of Jessop and coworkers demonstrated that DBU easily reacts with  $\text{CO}_2$  to form a stable adduct in presence of primary alcohol and water.<sup>[22,23]</sup> As already demonstrated for both  $\epsilon$ -caprolactone and trimethylene carbonate ring-opening polymerizations, a  $\text{ROCO}_2^{(-)}$ ,  $\text{DBU}\cdot\text{H}^{(+)}$  adduct – obtained from primary alcohol and DBU under 1 atm of  $\text{CO}_2$  – is not nucleophilic enough to initiate a polymerization process.<sup>[24]</sup> MA dimerization reactions were then performed under  $\text{CO}_2$  atmosphere to prevent poisoning anionic oligomerization from residual water by producing *in situ* a  $\text{HOCO}_2^{(-)}$ ,  $\text{DBU}\cdot\text{H}^{(+)}$  dormant salt species (Scheme 1).

As observed by Zhulin *et al.* who studied the dimerization of MA by the action of tri(*n*-butyl)phosphine in the absence of solvent,<sup>[11]</sup> the effectiveness of the bimolecular process at the first stage is sharply increased by the use of a high-pressure technique. To that reason, three different  $\text{CO}_2$  pressures (1, 20 and 40 bars) were evaluated for the synthesis of DMG ( $[\text{MA}]_0/[\text{DBU}]_0=1$ , 23 °C). Reactions performed at 1 and 40 bars were carried out for 15 hours while the one made under 20 bars of  $\text{CO}_2$  was stopped after 24 hours. While each reaction medium was analyzed by  $^1\text{H-NMR}$  though, SEC analysis was used as a preferred and easy characterization tool to highlight the selective formation of DMG. Each MA pure oligomer (dimer, trimer, etc.) presents a very specific  $^1\text{H-NMR}$  spectrum and their mixture appears really complex.<sup>[10]</sup> While the unambiguous observation of DMG by NMR is complicated, MA dimer presents an isolated chromatogram in SEC analysis. Figure 2 compares the SEC chromatograms of the three crude media to the



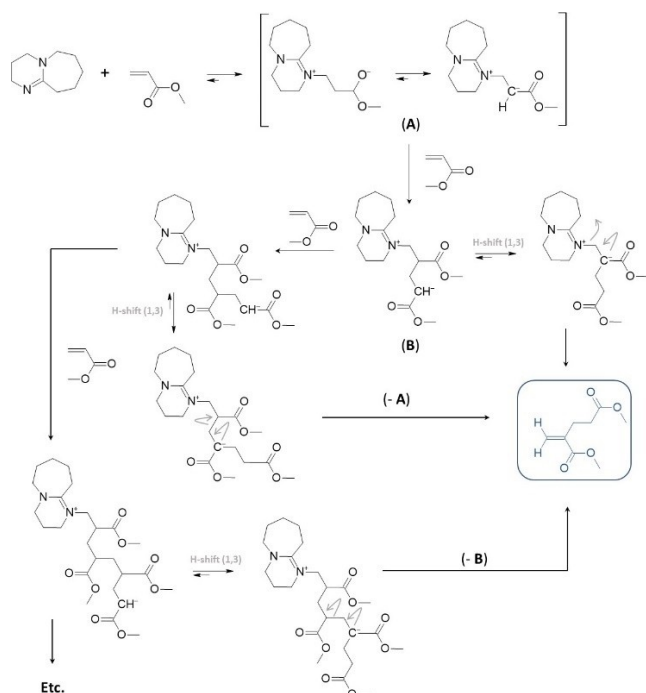
**Scheme 1.** Generation of "active" and "dormant" DBU salts by reaction of DBU and water in presence or not of carbon dioxide.



**Figure 2.** SEC chromatograms of crude media obtained under different pressures of  $\text{CO}_2$  ( $[\text{MA}]_0/[\text{DBU}]_0=1$ , 23 °C) and compared to isolated DMG and  $\text{HOCO}_2^{(-)}$ ,  $\text{DBU}\cdot\text{H}^{(+)}$  salt.

individual SEC analyses of the isolated pure MA dimer (see Figure S3, ESI) and the pre-synthesized  $\text{HOCO}_2^{(-)}$ ,  $\text{DBU}\cdot\text{H}^{(+)}$  ionic salt (see Figure S2, ESI). Under 1 bar of  $\text{CO}_2$ , the production of oligo-PMA is already drastically reduced and the selective production of DMG is clearly revealed. Increasing the pressure to 20 or 40 bars strongly reduces the presence of oligo-PMA improving the selective dimerization of MA. Interestingly, while an apparent selective dimerization occurs under a 20 bar pressure, oligomers of very low  $M_n$  ( $\sim 800 \text{ g}\cdot\text{mol}^{-1}$ , elution volume = 19 mL) are still observed after 15 hours under 40 bars. This might be attributed to the non-consistency of reaction times between both experiments, suggesting also that the production of DMG is not the result of a single  $\alpha$ -to- $\beta$  coupling of MA. This is in apparent contradiction to the report of Rauhut and Currier and suggests that DMG could also be produced by a series of transfer and scission reactions of the oligo-PMA produced from the initiating Michael adduct (A) (Scheme 2).

Experimental proofs of that rational pathway were found by analyzing the crude medium of a reaction carried out under 40 bars of  $\text{CO}_2$  over various intervals during a reaction time of 48 hours ( $[\text{MA}]_0/[\text{DBU}]_0=1$ , 23 °C, Figure 3). After 5 hours, the production of DMG is already accompanied by PMA of relatively high  $M_n$  ( $\sim 8000 \text{ g}\cdot\text{mol}^{-1}$ ). With time, both concentration and

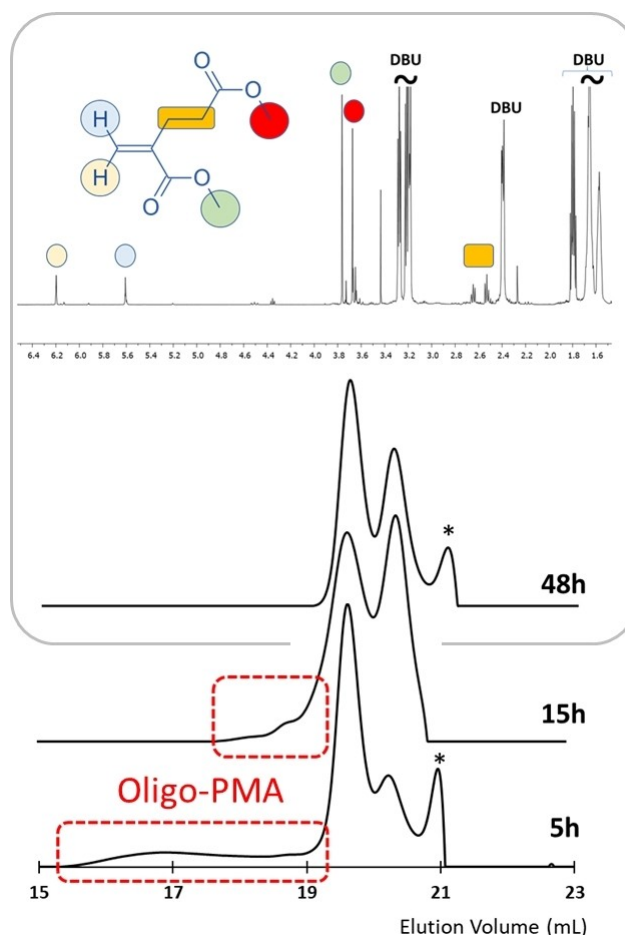


**Scheme 2.** Proposed mechanism for the preparation of DMG from MA and DBU.

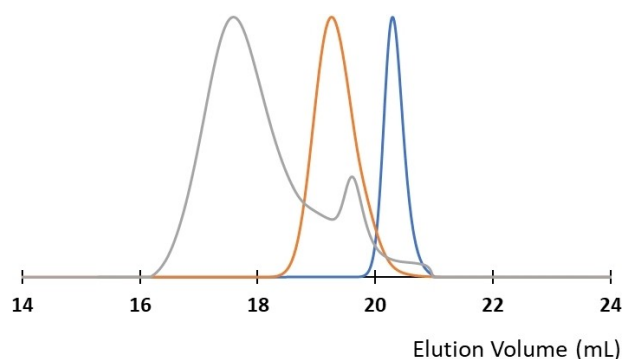
molar masses of the latter species fell off as the concentration of DMG increased leading to a quantitative production of MA dimer after 48 hours. The selective formation of DMG was attested by GC-MS and  $^1\text{H-NMR}$  analysis which gives clear evidence of the structure of the unsaturated dimer of MA by the presence of the well-split singlets of the  $\text{CH}_3$  protons of the two methyl esters (Figure 3, top and Figure S1).<sup>[21]</sup>

Because DBU is recognized as an efficient catalyst for transesterification reactions,<sup>[25,26]</sup> DMG containing DBU (salt) was directly subjected to a polycondensation copolymerization with  $\sim$  one equivalent of oligoethylene glycol ( $\text{MW} = 300 \text{ g}\cdot\text{mol}^{-1}$ , PEG300). The medium was kept under vacuum and was the object of successive thermal treatments at  $80^\circ\text{C}$  for 5 hours and  $110^\circ\text{C}$  for 12 hours. While  $^1\text{H-NMR}$  techniques attests that the evaporated product is methanol, the analysis of the medium evidenced that both DMG and PEG300 comonomers were inserted in the final poly(DMG-co-PEG) copolymer. Efficient crossover from PEG300 and DMG to the resulted step-growth-produced structure was confirmed by a major shift to a lower retention volume still containing some unreacted PEG300 ( $M_{n,\text{SEC}} = 2600 \text{ g}\cdot\text{mol}^{-1}$ , Figure 4). While the broad recorded dispersity of the sample ( $M_w/M_n = \mathcal{D}_M = 2.3$ ) is typical of a step-growth polymerization process, it could also be explained by competitive branching reactions of the unsaturated oligomers observed by  $^1\text{H-NMR}$  (See Figure S4, ESI).

In conclusion, we have demonstrated that DBU is an effective mediator for the head-to-tail dimerization of MA under moderated  $\text{CO}_2$  pressure (20 to 40 bars), in bulk condition and at room temperature. In presence of the amidine,  $\text{CO}_2$  transforms efficiently residual protic residues such as water in a



**Figure 3.** SEC chromatograms of DBU/MA crude media obtained after 5, 15 and 48 hours under 40 bars of  $\text{CO}_2$  ( $[\text{MA}]_0/[\text{DBU}]_0 = 1$ ,  $23^\circ\text{C}$ , \* solvent signal). Top:  $^1\text{H-NMR}$  analysis of the medium obtained after 48 hours.



**Figure 4.** Normalized SEC traces of DMG (blue line), PEG300 (orange line) and poly(DMG-co-PEG300) (grey line).

dormant organic salt unable to initiate the concomitant anionic polymerization of MA. In contradiction to the tri(*n*-butyl)phosphine-based Rauhut-Currier mechanism, we demonstrated that the selective production of MA dimer (DMG) issues from a succession of scission and transfer reactions leading quantitatively to the DMG molecule. DBU has also been used as

a transesterification agent in a step-growth copolymerization of DMG with a selected PEG300 diol.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

Research data are not shared.

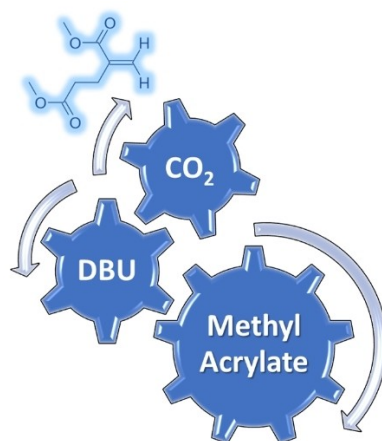
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## RESEARCH ARTICLE

The selective head-to-tail dimerization of methyl acrylate by associating DBU and CO<sub>2</sub> is presented. The synergistic combination mediates the process but also transforms protic impurities, such as water in dormant spectators, offering a good perspective to an industrially scalable method. The purity of the crude dimer is such that it could be directly involved in a step-growth copolymerization with a diol, using DBU as transfer agent.



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