Efficient and catalyst free synthesis of acrylic plastic precursors: methyl propionate and methyl methacrylate synthesis through reversible CO2 capture

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Green Chemistry

COMMUNICATION

Efficient and catalyst free synthesis of acrylic plastic precursors: methyl propionate and methyl methacrylate synthesis through reversible CO_2 capture

Santosh Govind Khokarale,*[a], Jyri-Pekka Mikkola[a, b]

Methyl propionate (MP) and methyl methacrylate (MMA) are considered as industrially important precursors upon large-scale acrylic plastic production. The existing industrial synthetic protocols of these precursors utilize expensive catalysts accompanied with toxic and explosive gases such as carbon monoxide, ethylene and hydrogen. Herein, we for the first time report highly selective, catalyst-free and room temperature synthesis of MP and MMA precursors through organic superbase involved reversible CO_2 capture approach. In short, initially equimolar mixture of organic superbase 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU) and methanol were reversibly reacted with molecular CO_2 and the obtained switchable ionic liquid, $[DBUH][MeCO_3]$ further reacted with an equivalent amount of propionic anhydride or methacrylic anhydride to form MP or MMA, respectively. These reactions were accomplished in different solvents such as DMSO and methanol whereupon, in case of methanol, separation of reaction products occurs from in-situ formed DBU derivatives such as [DBU][propionate] or [DBU][methacrylate]. In case of both MP and MMA synthesis, after use of methanol as a solvent, good recovery of alcoholic solution of esters were achieved where 85% and 92% yields of MP and MMA were obtained, respectively. The molecular DBU was recovered from its propionate and methacrylate salts using NaCl saturated alkaline solution. Further, the recovered MMA with methanol was polymerised to poly-MMA using a benzoyl peroxide induced free radical polymerisation process. The synthesis and separation of MP or MMA as well as recovery of DBU was monitored by NMR analysis. Hence, unlike DMSO, methanol not only performed as a regent in CO_2 capture and as a solvent media in MP, MMA and poly-MMA synthesis but also assisted in the recovery of DBU from the reaction mixture. Most importantly, here we represented a more efficient, safer and single solvent based alternative synthetic approach for the synthesis of acrylic plastic precursors MP or MMA compared to existing industrial methods. Also, no toxic or expensive catalysts were required.

1. Introduction

Methyl methacrylate (MMA) is an industrially important monomer/precursor for the synthesis of various acrylate based plastics (e.g. poly-methylmethacrylate, PMMA, MMA-butadiene copolymer) where currently 75 % of world's MMA consumption is in acrylic plastic production [1]. MMA is also widely used to produce resins, plastic coatings, paints, adhesives, and other important fine chemicals [1]. Acrylic plastic or PMMA is a optically clear thermoplastic material and very versatile because of its durability, impact, strength, colour and pattern possibilities and hence has enormous applications in our day-to-day life including automotive, construction, retail and electronics, aerospace industry, paints and coatings etc. [2]. Considering the huge world demand of acrylic plastic and hence MMA, enormous amounts of MMA is produced in practice through various industrial processes. Among these

processes, acetone-cyanohydrin process (ACH sulfo process, C_3 route), isobutene oxidation (C_4 route) and alpha process (C_2 route) are sharing the major part of global MMA production [3]. Recently, Evonik (leading industry for speciality chemicals) as well as Gao et al. developed a new process for the production of MMA (LiMA, leading to methacrylate) following a route involving direct oxidative esterification of methacrolein, a condensation product between propionaldehyde and formaldehyde. This newly developed process is more simple as it is accompanied with high raw material availability, less environmental impacts (reduction in CO_2 emissions by 40 %), efficient and selective catalysts and feasible process parameters (e.g. reaction temperature $\leq$ 100 °C) compared to existing industrial processes [4a,b]. Even though all these processes are playing a vital role in MMA production, each of these processes have their own drawbacks such as environmentally hazardous waste production or use of toxic and flammable reagents etc. Hence, both in industry and in academia researchers are focusing to improve the current processes and/or inventing new and more environmentally friendly processes for the MMA synthesis [3]. In these regards, following the principles of "Green Chemistry", such as use of less

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toxic reagents as well as less production of waste in downstream processes are the main targets currently under rigorous study.

As already mentioned, the Alpha process (C_2 process) developed by Lucite international is another well-established and industrially applied process for MMA production [5]. This two-step synthetic protocol involves the synthesis of methyl propionate (MP) by methoxycarbonylation of ethylene followed by condensation of MP with formaldehyde to MMA (reaction scheme 1) [6a-d]. Following the Alpha process, the industries in Singapore (Alpha 1, 2008, Lucite international) as well as in Saudi Arabia (Alpha 2, 2017, Mitsubishi Chemical Corporation and Saudi Basic Industries Corporation) currently produce 100, 000 tons and 250, 000 tons of MMA per annum, respectively.
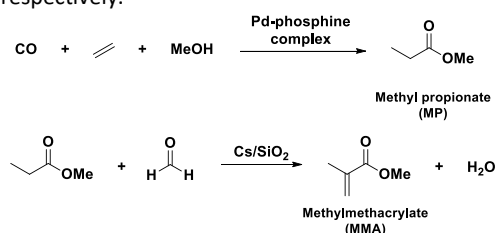
Scheme 1. The Alpha process, two step MP synthesis: a) Methoxycarbonylation of ethylene to MP and, b) Condensation of MP with formaldehyde to MMA

Even though the Alpha process is well established upon MMA production, the synthesis of MP in the first step of the process is still coupled with major drawbacks such as the use of expensive Pd-phosphine homogeneous catalyst and handling of poisonous carbon monoxide gas. To overcome these drawbacks, several processes have been developed during the last decade aiming at either recycling of the expensive catalyst or a new synthetic approach for MP synthesis involving biomass derived precursors and cheaper heterogeneous catalysts.
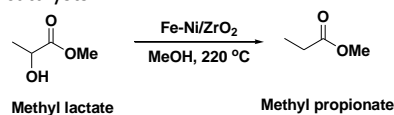

Scheme 2. Hydrodeoxygenation of biomass derived methyl lactate to MP.

Riisager et al. used a Brønsted acid ionic liquid as an efficient reaction media for methoxycarbonylation of ethylene to MP where the ionic liquid was involved in the stabilisation as well as separation of the expensive Pd-complex from the reaction mixture via a biphasic reaction approach [7 a,b]. The same authors further explored this ionic liquid involved metal complex system in the vapour phase synthesis of MP by developing a supported ionic liquid phase (SILP) technology. In both liquid as well as vapour phase approaches, a higher than ≥ 99 % yield of MP was obtained as the used Pd-phosphine complex was highly chemo-selective for MP instead of the alternative copolymerised products. On the other hand, in order to avoid the use of carbon monoxide as well as expensive Pd-phosphine catalyst upon MP synthesis, Shunmugavel et al. developed a heterogeneous catalyst based approach for the MP synthesis where cheaper base metal catalysts were used for selective hydrodeoxygenation of biomass derived methyl lactate with 77% MP yield, at 220 °C in 12 hour (scheme 2) [8]. Even though these new processes are promising to simplify the MP synthesis, still the use of expensive catalysts as well as ionic liquids along with poisonous carbon monoxide gas in case of the Alpha process and high temperature reaction approach, slow reaction kinetics and use of explosive H_2 gas in hydrodeoxygenation of methyl lactate influence

the overall economy as well as the safety of these processes. Hence, catalytic processes with mild reaction conditions and neutral gas atmosphere are comparatively safe upon industrial scale production. Furthermore, catalyst free synthesis of the desired product under mild reaction conditions is the preferred alternative for several industrial processes.

Reversible CO_2 capture using strong organic bases or superbases such as amidines and guanidines, in addition with various proton donors such as alcohols, water, alkanolamines etc. is not only an elegant technique for CO_2 capture and storage (CCS) but it provided a new solvent media in the form of special types of ionic liquids as switchable ionic liquids [9a-c]. Mikkola et al. have used these types of ionic liquids successfully as a solvent media upon biomass pretreatment such as wood delignification [10a-c]. Apart from it, recently similar reversible CO_2 capture approach through organic superbase involved process was applied in the catalyst free synthesis of cellulose derivatives such as cellulose esters under mild reaction conditions [11a-f]. Here, initially rapid and efficient dissolution of crystalline cellulose was attained through its interaction with an organic superbase 1, 8-diazabicyclo-[5.4.0]-undec-7-ene, DBU and molecular CO_2 [12a, b]. The obtained soluble cellulose further reacted with various alkyl anhydrides to form its corresponding ester derivatives. Apart from cellulose ester synthesis, Liu et al. discovered that lower esters such as methyl acetate can also be synthesised following this reversible CO_2 capture approach. In this case, the authors noted that during the cellulose ester synthesis, as a side reaction, the previously synthesised [DBUH][MeCO$_3$] formed due to the interaction of DBU and MeOH with CO_2 which also reacted with acetic anhydride and formed methyl acetate [11b]. Hence, under mild reaction conditions and under catalyst free reaction conditions, various alcohols including biomolecules can be derivatized to their esters using efficient organic superbase involved reversible CO_2 capture reaction approach.

Mimicking the above described ester synthesis protocol, in this report we are for the *first time* introducing a catalyst free synthesis of MP and MMA, occurring at room temperature through reversible CO_2 capture by an organic superbase DBU (reaction scheme 3). During the actual synthesis, initially [DBUH][MeCO$_3$], (a switchable ionic liquid) was synthesised through interaction of equimolar mixture of DBU and methanol with molecular CO_2. In the second step, the formation of MP or MMA was achieved through interaction of [DBUH][MeCO$_3$] with equimolar amounts of propanoic (R = CH$_2$-CH$_3$) or methacrylic anhydride (R = C(CH$_3$)=CH$_2$), respectively. The molecular CO_2 was released in the second step along with the formation of [DBUH][propanoate] or [DBUH][methacrylate] as a by-product upon reaction during MP or MMA synthesis, respectively. The progress of both steps, i.e. process of reversible CO_2 capture and MP or MMA synthesis, were monitored by NMR analysis. The separation of reaction products such as MP or MMA from the reaction mixture, recovery of molecular DBU as well as polymerisation of recovered MMA to poly-MMA is also described in this report.
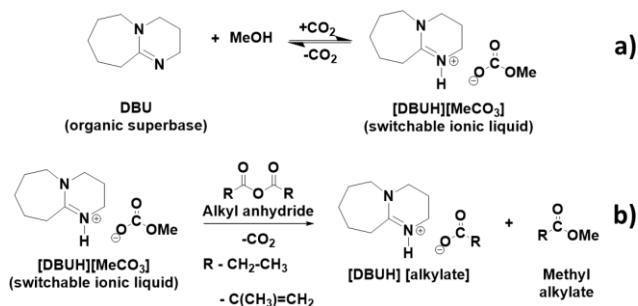
Scheme 3. a) Switchable ionic liquid synthesis and, b) MP or MMA synthesis

2. Experimental
2.1 Chemicals and methods
2.1.1 Chemicals
1,8-Diazabicyclo-[5.4.0]-undec-7-ene (DBU, ≥99.0%, GC analysis), propanoic anhydride (≥99.0%), methyl propionate (≥99.0%), methacrylic anhydride (94.0%), methyl methacrylate (99.0%), d⁶-DMSO (anhydrous, 99.9 atom% D and $CDCl_3$ (99.96 atom% D) were purchased from Sigma Aldrich while methanol (≥99.0%), acetone (≥99.0%) and dimethyl sulfoxide (≥99.0%) were purchased from VWR chemicals and used further without purification. CO_2 and ^{13}C enriched CO_2 gas bottles (>99.99%) were obtained from AGA AB (Linde Group) and used without further purification.

2.1.2 NMR and FTIR analysis
The composition of the reaction mixtures was confirmed by means of NMR analysis using the Brucker's Avance 600 MHz instrument. In these analyses, as per requirement, either glass capillary filled with D_2O or DMSO-d⁶ or $CDCl_3$ were used as internal standards. The obtained data was further processed with TopSpin 3.2 software. The Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) technique was used for the analysis of alcoholic solutions of MP and MMA by Bruker Vertex 80v FT-IR spectrometer equipped with a DTGS detector.

2.2. Synthesis and separation of MP and MMA and recovery of DBU

2.2.1 Synthesis of [DBUH][MeCO₃] or SIL with and without dimethyl sulfoxide (DMSO) solvent
The [DBUH][MeCO₃] (SIL) was synthesized via an interaction of CO_2 molecule with DBU and methanol with or without DMSO. During the actual synthesis, CO_2 gas was bubbled under stirring in the DMSO solution containing equimolar amounts of DBU and methanol or in alcoholic solution of DBU (50 vol. % of DBU in methanol), at room temperature. In both cases, pale yellow clear solutions were obtained and their compositions were further analysed by NMR analysis. Furthermore, the SIL was also synthesized with ^{13}C isotope enriched CO_2 molecule (tracer technique). The NMR analysis was carried out with D_2O filled in a glass capillary swimming in the reaction mixture with DMSO solvent or with DMSO-d⁶ for reaction with methanol solvent.

2.2.2. Synthesis of MP or MMA
Equimolar amounts of anhydride precursors such as propionic or methacrylic anhydride based on DBU amounts were slowly added under stirring to previously synthesized DMSO or alcoholic solution of SIL, at room temperature. The reaction mixture was kept under stirring for 1h at room temperature and the formation of MP and MMA were further confirmed by means of NMR analyses. In case of

reaction mixtures containing DMSO as a solvent, the NMR analysis was performed using a capillary containing D_2O as an internal standard. Upon use of reaction mixture with MeOH as a solvent, the NMR analysis was carried out with DMSO-d⁶ as the internal standard. The types of chemical species formed upon synthesis of MP or MMA are depicted in Fig. 1. Further MP was also synthesized in DMSO solution containing the ^{13}C-SIL.

2.2.3 Separation of MP or MMA from reaction mixture
The separation of MP or MMA and recovery of DBU was performed only for the reaction proceeding with alcoholic solutions of SILs. After complete conversion of $MeCO_3^-$ (confirmed by NMR analysis), MP or MMA along with the excess methanol was separated from the [DBUH][propionate] or [methacrylate] by high vacuum distillation at 40 °C. In order to avoid the loss of MP or MMA and methanol, the reservoir used for the collection of MP or MMA with methanol was kept in a cold trap containing dry ice (solid CO_2) and acetone. The purity of the obtained products MP or MMA with methanol as well as remaining [DBUH][propionate] or [methacrylate] were confirmed by NMR analysis (with DMSO-d⁶ as an internal standard).

2.2.4 Yield of MP and MMA
The amount of alcoholic solution of MP or MMA recovered after separation from the reaction mixture was interpreted by Equation 1, where V_R and V_E represent the recovered and theoretically expected volumes of alcoholic solution of MP or MMA, respectively. Further, the yields of MP or MMA were obtained by using Equation 2, where n_R and n_E denote the number of moles of recovered and theoretically expected number of moles of MP or MMA, respectively. The recovered and expected moles of MP or MMA were calculated using the results from gas chromatography (GC) in an Agilent 7820 N instrument equipped with a HP-5 column (30 m length, 0.3 mm internal diameter, and 0.25 µm of film thickness) and the FID detector. Helium gas was used as a carrier gas. The GC injection port and detector temperature were set at 300 °C. The temperature programme during analysis was maintained as follows: Initially the column temperature was maintained at 50 °C for 1 min and then a temperature ramp from 50 °C to 100 °C with a heating rate of 4.5 °C/min was commenced. After reaching 100 °C, temperature was further increased with rate of 20 °C/min to 300 °C and the temperature was held at this temperature for 7 min. During the actual MP or MMA synthesis, 3 ml of 50 vol. % of alcoholic solution of DBU was used.. Since we know the amount of DBU in the solution, corresponding amount of MP or MMA should form in the reaction mixture. During the calibration, various amounts of MP or MMA were mixed with mesitylene (the internal standard) and further diluted with DMSO. The obtained calibration curves are shown in the supporting information S4. Finally, the yield of MP or MMA were calculated in the recovered alcoholic solutions with the help of the calibration curves and Equation 2.

$$\% \text{ Amount of alcoholic solution of MP or MMA recovered} = \frac{V_R}{V_E} \times 100 \quad ....(1)$$

$$\% \text{ Yield of MP or MMA} = \frac{n_R}{n_E} \times 100 \quad ....(2)$$

2.2.5 Synthesis of poly-MMA from recovered MMA
The obtained MMA with methanol was further converted to poly-MMA by free radical polymerisation using benzoyl peroxide as the radical initiator. The reaction mixture containing an alcoholic solution of MMA (in methanol) and the free radical (5 wt. % based on MMA amount) were refluxed at 70 °C. The reaction was quenched

after 4h as highly viscous liquid formation was observed. After cooling of the reaction mixture, a white precipitate was slowly settling at the bottom of the reaction flask. To purify the product, the white precipitate was further dissolved by addition of minimum amount of acetone and the product was further re-precipitated by addition of excess of methanol under vigorous stirring. The obtained white precipitate was separated from the reaction mixture by filtration and washed 3-4 times with methanol. After drying overnight, at room temperature, the white product was further dried in vacuum for 3 h at 70 °C and its purity as poly-MMA was confirmed by NMR analysis (with $CDCl_3$ as an internal standard).

2.2.6 Recovery of DBU

The DBU was recovered from [DBUH][propanoate] or [methacrylate] by using alkaline NaCl saturated aqueous solution following a previously reported procedure [11b, 11f]. Initially, saturated NaCl aqueous solution was prepared by mixing NaCl in water under stirring and the required amount of solution was taken to make 4 wt. % solution of NaOH in a NaCl saturated solution. This alkaline NaCl saturated solution was further added to [DBUH][propanoate] or [methacrylate] and the mixture was stirred for 30 min. at room temperature. The DBU was extracted with ethyl acetate and separated from the aqueous phase by using a separating funnel. The DBU was obtained from organic phase after removing ethyl acetate by rotation evaporator under high vacuum and its purity was confirmed by NMR analysis. The recovery percentage (weight %) of DBU was calculated from the recovered amount and initial amount used for CO_2 capture in the reaction.

3.   Result and discussion

3.1.   Synthesis of MP with and without DMSO solvent and recovery of DBU

3.1.1.   Synthesis of MP with DMSO solvent

The reversible CO_2 capture by DBU along with equivalent amounts of methanol in a DMSO solvent was performed and the transformation of molecular DBU to its ionic form i.e. [DBUH][MeCO_3] or SIL was confirmed by ^{13}C NMR analysis. As shown in Fig. 2, after the SIL formation the peaks belonging to the carbon atoms of DBU at positions 6 and 9 got shielded by 5-6 ppm whereas the peak belonging to carbon atom at positon 7 got de-shielded by 5 ppm. Also, the peaks related to methyl group in the free methanol disappeared at 47.44 ppm and new peaks for methyl group and carbonyl carbon in $MeCO_3^-$ anion were observed at 50.06 and 155.97 ppm, respectively. Hence, it is evident that the SIL got formed after equivalent interaction of DBU, methanol and CO_2 with each other. Further, the formation of SIL was also confirmed by ^{1}H NMR analysis (supporting information S1-a and b). Similar observations based on ^{13}C NMR analysis for the formation of SIL have also been described in previously reported articles [11b].
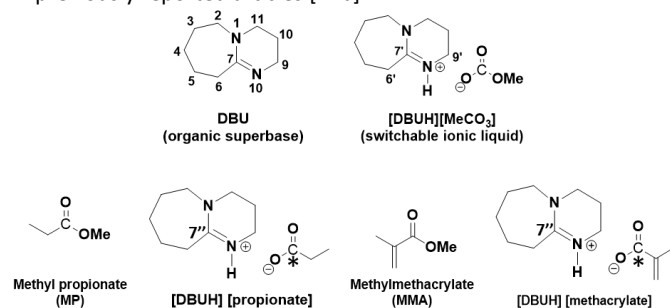

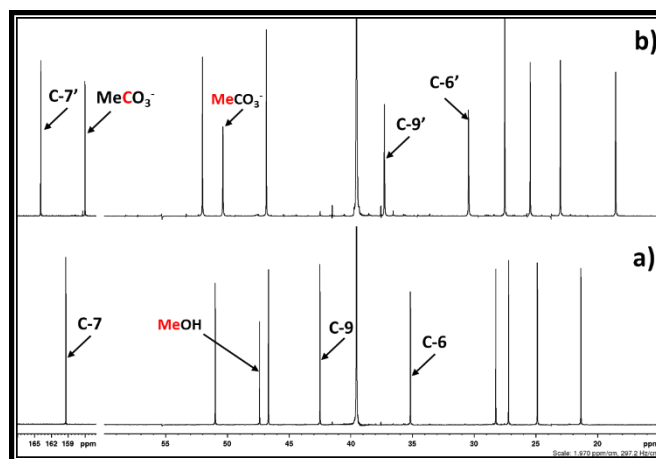**Figure 1.** Chemical species formed in MP and MMA synthesis

Figure 2. ^{13}C NMR spectra for the synthesis of [DBUH][MeCO_3], SIL from DBU, methanol and CO_2 in DMSO. a) DBU and MeOH, and b) [DBUH][MeCO_3].

The MP synthesis process further continued whereupon propionic anhydride (based on amount of DBU or methanol used) was added in DMSO solution of SIL. After addition of propionic anhydride, the immediate release of molecular CO_2 was observed and as represented in the reaction scheme 3, the interaction of SIL with the anhydride precursor was confirmed through release of molecular CO_2. After stirring the reaction mixture at room temperature for 1h, the ^{13}C NMR analysis was performed to confirm the formation of MP. As shown in Fig. 3, after addition of an equivalent amount of propionic anhydride, the signal related to the $MeCO_3^-$ anion at 155.97 ppm disappeared and the peak related to carbonyl carbon in MP appeared at 174 ppm. Further, the formation of MP was confirmed by comparing the ^{13}C NMR spectra of the reaction mixture with commercially available MP. In case of in-situ formed [DBUH][propionate], the signal belongs to sp^2-hybridised carbon i.e. C-7'' in DBUH[+] cation and carbonyl carbon in [propionate] anion are observed at 165.31 and 177.34 ppm, respectively. ^{1}H NMR analysis of the reaction mixture was also carried out and the spectra confirmed the formation of MP after interaction between the SIL and propionic anhydride (supporting information S1-c and d).

Now, in order to confirm the origin of the molecular CO_2 released during the MP synthesis, ^{13}C isotope enriched CO_2 was used. Initially, the SIL was prepared after interaction of equimolar mixture of DBU and methanol with ^{13}C-CO_2. The resultant SIL was further analysed by means of ^{1}H and ^{13}C as well as two-dimensional NMR analysis. As shown in Fig. 3-b, the NMR spectrum of SIL formed with ^{13}C-CO_2 gave rise to a high intensity of carbonyl carbon in the $MeCO_3^-$ anion compared to C-7' of the protonated DBU molecule. As shown in the reaction scheme 3-a, molecular CO_2 reacts during the SIL formation through chemical interaction with the in-situ formed methoxide anion.
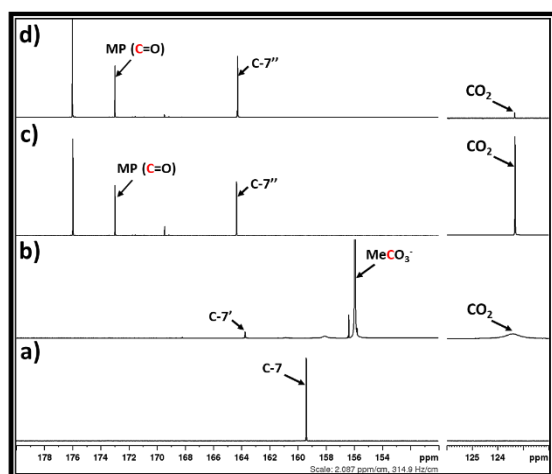
Figure 3. ^{13}C NMR spectra of a) DBU and MeOH, b) [DBUH][MeCO$_3$] with ^{13}C-CO$_2$ reaction mixture in DMSO: MP and [DBUH][propionate] obtained after reaction of propionic anhydride with c) ^{13}C-[DBUH][MeCO$_3$] and d) [DBUH][MeCO$_3$]

Further, to emphasize the chemical interaction of CO$_2$ and methoxide anion during the SIL formation, two-dimensional long range ^1H-^{13}C HMBC (Heteronuclear Multiple Bond Correlation) NMR analysis of both reaction mixtures containing SIL formed with the ^{13}C-CO$_2$ and "normal" CO$_2$ was carried out. As shown in Fig. 4-a, the correlation peak observed at the position 3.21/156.12 ppm is associated with a long range correlation between protons and carbonyl carbon in the MeCO$_3^-$ anion of the SIL. Also, similar observation was made for the SIL obtained with ^{13}C-CO$_2$ (Fig. 4-b). Hence, the NMR analysis proves that during the SIL synthesis the CO$_2$ molecule is chemisorbed upon the MeCO$_3^-$ anion formation. After the addition of propionic anhydride in a DMSO solution of the SIL, the MP and [DBUH][propionate] formed upon release of molecular CO$_2$. As shown in Fig. 3-c, after addition of propionic anhydride, the signal at the position 156.12 ppm disappeared while a new intense signal, at the position 123.4 ppm, appeared. The new signal belongs to molecular CO$_2$ [13]. As shown in Fig. 3-c and d, respectively, the signal for molecular CO$_2$ obtained after MP synthesis from ^{13}C-[DBUH][MeCO$_3$] has a very intensity compared to the one when "normal" (non-^{13}C) CO$_2$. Also, no high intensity signal appeared for ^{13}C enriched CO$_2$ containing species between 160 and 180 ppm after the MP synthesis (Fig. 3-c). Hence, we can conclude that the molecular CO$_2$ originated from the MeCO$_3^-$ anion upon the MP synthesis process.
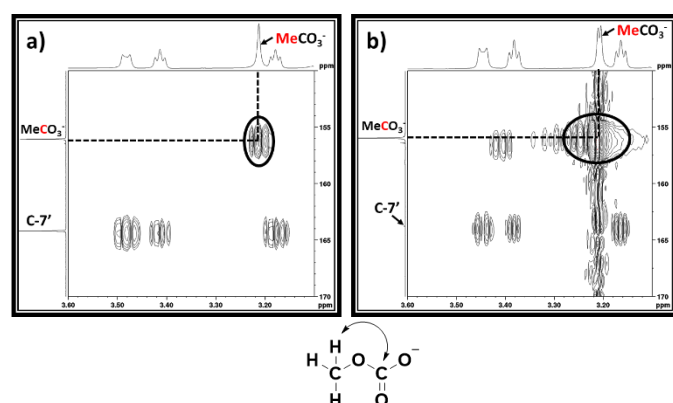
As [DBUH][propionate] formed in the reaction mixture, we can assume that the [DBUH]$^+$ cation might not interfere in the MP formation process. On the other hand, it seems that the formation of MP preceded after interaction between MeCO$_3^-$ anion and propionic anhydride. In the previous section we have shown that the ester synthesis proceeds through the release of CO$_2$ after the decomposition of the MeCO$_3^-$ anion. However, a release of molecular CO$_2$ after addition of propionic anhydride and further interaction of methoxide anion with propionic anhydride was still not confirmed. As already mentioned, the formation of MP after interaction of propionic anhydride with SIL is mimicked in the cellulose ester synthesis process. In the previous reports, concerning the synthesis of these cellulose derivatives is not adequately explained since the interaction between cellulose alkyl carbonate anion (formed after interaction between cellulose, DBU and CO$_2$) and alkyl anhydride occurs before ester formation via the release of CO$_2$. Hence, in MP synthesis one needs to understand the release of molecular CO$_2$ from MeCO$_3^-$ anion after addition of propionic anhydride. The reaction scheme 4 represents a plausible interaction between MeCO$_3^-$ anion and propionic anhydride during MP synthesis. As shown in reaction scheme 4a, it is possible that the MeCO$_3^-$ anion is in equilibrium with the methoxide anion and molecular CO$_2$ and the equilibrium was not disturbed until the addition of propionic anhydride. However, after the addition of propionic anhydride this equilibrium seems to be disturbed whereupon the methoxide anion got consumed via its interaction with the anhydride molecule (scheme 4b). Therefore, this might give rise to the release of CO$_2$ in the reaction mixture.
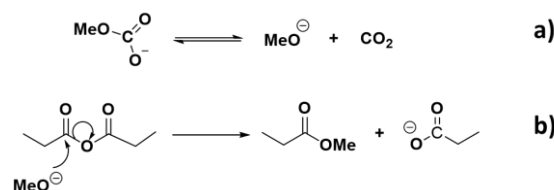
Scheme 4: Plausible mechanism for MP synthesis.

Now, as shown in Fig. 5, the MP formed after disappearance of MeCO$_3^-$ anion in the reaction mixture. In order to confirm this, different equivalents such as 0.5, 0.8 and 1 (on the basis of DBU or methanol) of propionic anhydride were added to the DMSO solution of the SIL. The formation of MP was monitored with ^{13}C NMR analysis and the obtained spectra are summarized in Fig. 6. After regular addition of propionic anhydride, the signals belonging to the MeCO$_3^-$ anion steadily decrease while the signals related to the MP and propionate anion increased accordingly. Hence, the formation of MP in the reaction mixture can be monitored by NMR analysis on the basis of signals appearing for the MeCO$_3^-$ anion. Considering this aspect, as shown in Fig. 5 a and b, the MeCO$_3^-$ anion got completely converted to MP.

Figure 4. ^1H-^{13}C HMBC NMR spectra of [DBUH][MeCO$_3$] in DMSO obtained with a) CO$_2$ and b) ^{13}C-CO$_2$.
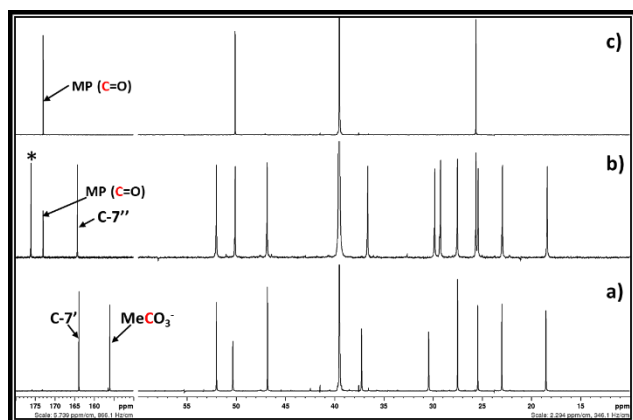
Figure 5. ^{13}C NMR spectra for the synthesis of MP from DMSO solution of [DBUH][MeCO₃] and propionic anhydride, a) [DBUH][MeCO₃], b) reaction mixture in DMSO: MP and [DBUH][propionate] and, c) commercially available MP (peak represented by the asterisk belongs to carbonyl carbon in [DBUH][propionate])

The separation of MP from the reaction mixture along with recovery of the DMSO as well as DBU superbase are equally important aspects if process economy is concerned. Considering the lower boiling point of MP (79.8 ^{O}C), its separation from the reaction mixture is possible through a low temperature distillation process. On the other hand, DMSO has a boiling point of 189 ^{O}C and hence its recovery from the reaction mixture is more energy-intensive compared to MP. The presence of DMSO in the reaction mixture can also influence the recovery of DBU. Therefore, instead of searching new techniques for DMSO separation from reaction mixture, here we decided to replace the DMSO with excess of methanol in the starting reaction mixture during SIL synthesis and similar alcoholic solution of SIL was used further for MP synthesis.
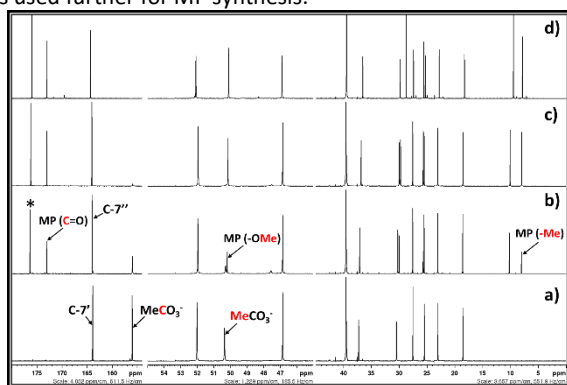

Figure 6. ^{13}C NMR spectra for the synthesis of MP from DMSO solution of [DBUH][MeCO₃] and propionic anhydride, a) [DBUH][MeCO₃], reaction mixture containing DMSO, SIL and, b) 0.5 c) 0.8 and d) 1 eq. propionic anhydride.

3.1.2. Synthesis of MP in methanol (without DMSO)
The SIL in methanol was prepared after bubbling CO_2 in DBU and a methanol mixture containing 50 vol. % of DBU. The formation of [DBUH][MeCO₃] was confirmed by ^{13}C NMR analysis and the obtained spectra are summarized in supporting information S2. Further an equivalent amount of propionic anhydride (based on DBU) was added dropwise at room temperature to the reaction mixture an immediate CO_2 release was observed. After stirring for

1h, the formation of MP was confirmed by ^{13}C NMR analysis. As shown in Fig. 7, similar to previous experiments where MP was synthesized in DMSO, a complete transformation of MeCO₃⁻ anion to MP was also observed in the alcoholic solution. Hence, the synthesis of MP following reaction scheme 3 is not only limited to a polar non-protic solvent such as DMSO, but it can proceed in polar protic solvents like alcohol i.e. in this case methanol. Further, methanol not only performed as a solvent and reagent for CO_2 capture but also served as a role of solvent media to accomplish the MP synthesis process.
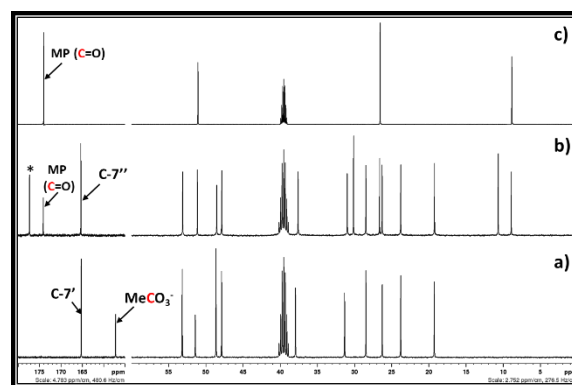

Figure 7. ^{13}C NMR spectra for the synthesis of MP from alcoholic solution of [DBUH][MeCO₃] and propionic anhydride, a) [DBUH][MeCO₃], b) reaction mixture in MeOH: MP and [DBUH][propionate] and, c) commercially available MP, (peak represented by the asterisk belongs to carbonyl carbon in [DBUH][propionate]).

3.1.3. Separation of MP from reaction mixture and recovery of DBU
The DMSO free synthesis of MP was carried out to replace the expensive DMSO and to ease the separation of MP from the reaction mixture as well as the recovery of DBU. Considering the lower boiling point of MP and methanol, their separations from the reaction mixture were performed under high vacuum where both MP and methanol were collected in a cold trap kept in acetone-dry ice solution. The separation of reaction components i.e. MP, methanol and [DBUH][propionate] were confirmed by ^{13}C NMR analysis. As shown in Fig. 8, the pure form of MP and methanol got separated from the [DBUH][propionate] following high vacuum distillation. ^{1}H NMR spectra as well as FTIR spectra of the recovered alcoholic solution of MP are shown in supporting information S5 and S7-a, respectively. Further, 93 % recovery of alcoholic solution of MP was achieved after distillation whereas 85 % yield of MP was obtained after distillation.

The recovery of molecular DBU from its ionic form i.e. from [DBUH](propionate] was performed using alkaline NaCl saturated aqueous solution. Similar alkaline solvent system previously used for the deprotonation of DBU from its ionic forms during cellulose esters [11b, 11f]. Even though this method was not well optimized, it is frequently used to recover DBU from its ionic forms. As described in the experimental section, after the treatment of [DBUH][propionate] with alkaline NaCl saturated solution, molecular DBU was extracted from alkaline solution with ethyl acetate. The DBU was further recovered after separation of ethyl acetate by distillation and its purity was confirmed by ^{13}C NMR analysis. As shown in supporting information S8, the purified form of

molecular DBU was obtained with 89 wt.% recovery. Hence, MP synthesis can be proceed with the recovery of DBU superbase.
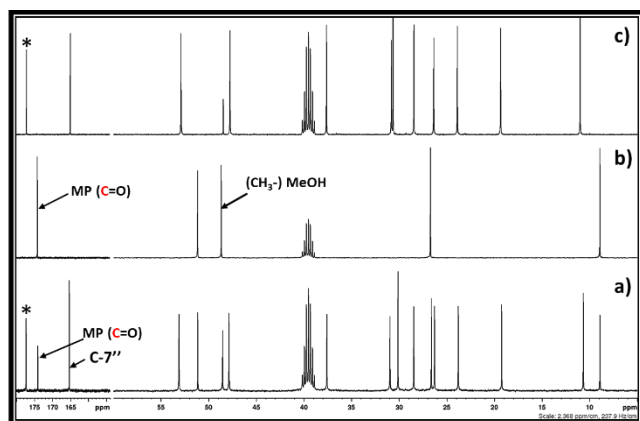

Figure 8. ^{13}C NMR spectra for the separation of MP and methanol from [DBUH][propionate], a) reaction mixture in MeOH: MP and [DBUH][propionate], b) recovered MP and MeOH from reaction mixture and, c) recovered [DBUH][propionate].

3.2. Synthesis of methylmethacrylate (MMA) in with and without DMSO solvent and recovery of DBU

3.2.1. Synthesis of MMA with DMSO

The MMA synthesis was proceeded with similar experimental procedure that used for MP synthesis using methacrylic anhydride as the anhydride precursor. In this case, methacrylic anhydride was added to the previously synthesised DMSO solution of SIL and the reaction mixture was stirred for 1h. ^{13}C NMR analysis of the reaction mixture was further performed to confirm the formation of MMA. As shown in Fig. 9, ^{13}C NMR spectra demonstrates that after the addition of methacrylic anhydride, the $MeCO_3^-$ anion got completely consumed and, accordingly, MMA formed in the reaction mixture and signal belonging to the carbonyl carbon in MMA appeared at 167.39 ppm. Further, the formation of MMA was confirmed after comparing the NMR spectra of the reaction mixture and commercially available MMA. The formation of [DBUH][methacrylate] was also confirmed by NMR analysis where sp^2-hybridised carbon i.e. C-7'' in [DBUH] cation and carbonyl carbon in methacrylate anion appeared at 165.40 and 171.64 ppm, respectively. ^{1}H NMR spectra shown in supporting information S3 also confirmed the formation of MMA as a result of the interaction between [DBUH][MeCO₃] and methacrylic anhydride.
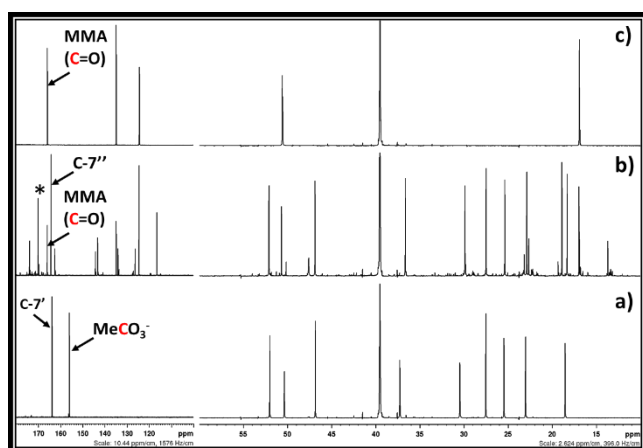

Figure 9. ^{13}C NMR spectra for the synthesis of MMA from DMSO solution of [DBUH][MeCO₃] and methacrylic anhydride, a) [DBUH][MeCO₃], b) reaction mixture in DMSO: MMA and [DBUH][methacrylate] and, c) commercially available MMA (peak represented by the asterisk belongs to carbonyl carbon in [DBUH][methacrylate]).

3.2.2 Synthesis of MMA in methanol (without DMSO), separation of MMA and recovery of DBU

Similar to MP synthesis, the process of synthesis of MMA was also performed in methanol. Initially, the SIL was synthesised in methanol followed by the addition of an equivalent amount of methacrylic anhydride to synthesise MMA. As shown in Fig. 10, after comparing the NMR spectra of the reaction mixture with commercially available MMA, it was confirmed that MMA formed after interaction of SIL with the methacrylic anhydride in methanol. After complete conversion of the $MeCO_3^-$ anion, the MMA and methanol were separated from the reaction mixture under high vacuum and [DBUH][methacrylate] was collected to recover the DBU superbase.
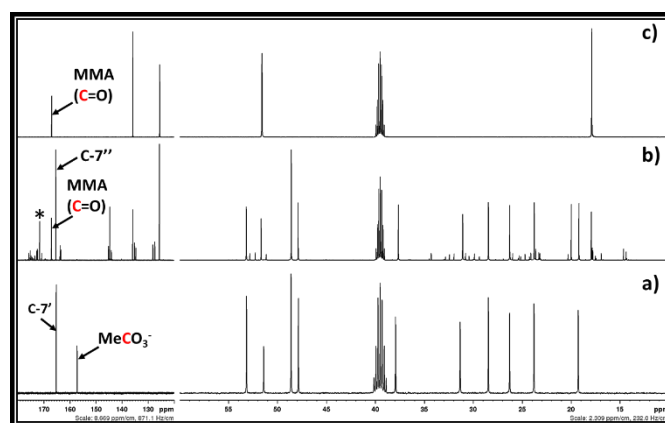

Figure 10. ^{13}C NMR spectra for the synthesis of MMA from alcoholic solution of [DBUH][MeCO₃] and methacrylic anhydride, a) [DBUH][MeCO₃], b) reaction mixture in MeOH: MMA and [DBUH][methacrylate] and, c) commercially available MMA (peak represented by the asterisk belongs to carbonyl carbon in [DBUH][methacrylate]). (peak represented by asterisk is belongs to carbonyl carbon in [DBUH][methacrylate]).

The separation of MMA and methanol from the reaction mixture was further confirmed by NMR analysis. As shown in Fig. 11, it is possible to separate MMA with methanol from the [DBUH][methacrylate]. Further, the ^{1}H NMR analysis of the separated alcoholic solution of MMA was also carried out and the results are summarised in supporting information S6. The purity of the recovered alcoholic solution of MMA was also confirmed by FTIR analysis and the spectra can be found in supporting information S7-b. 10% of the alcoholic solution of MMA was lost due to the evaporation of both MeOH and MMA during the distillation. In the recovered distillate, 92 % yield of MMA was obtained. Further, the DBU was recovered from [DBUH][methacrylate] alkaline and NaCl saturated aqueous solution with 82 wt.% of recovery and its purity was confirmed by NMR analysis (supporting information S9). Hence, similar to MP synthesis, methanol can be used as a reagent as well as solvent system upon synthesis of MMA.

Hence, catalyst free synthesis of both MP and MMA are described in this report. The reaction proceeds under mild reaction conditions and in a single solvent system. In industrial processes, both MP and MMA syntheses are usually dependent on the availability of different toxic and expensive reagents as well as catalysts. Also, these processes are often accompanied with harsh reaction conditions such as high temperature, pressure and explosive and toxic gas environments. On the other hand, the reagents used in the process for both MP and MMA synthesis such as propionic and methacrylic anhydrides, methanol and CO_2 gas are less expensive and toxic as well as easily available compared to reagents currently used in industrially applied processes. The organic superbase used, i.e. DBU, is comparatively expensive compared to other reagents used in this process. However, as shown, the DBU can be recovered at the end of the process in its pure form using a cheap alkaline solvent treatment. Hence, in overall, the method developed for the synthesis of MP and MMA can be considered as a more sustainable and greener compared to mainstream industrial processes and can be explored at pilot as well as industrial scale.
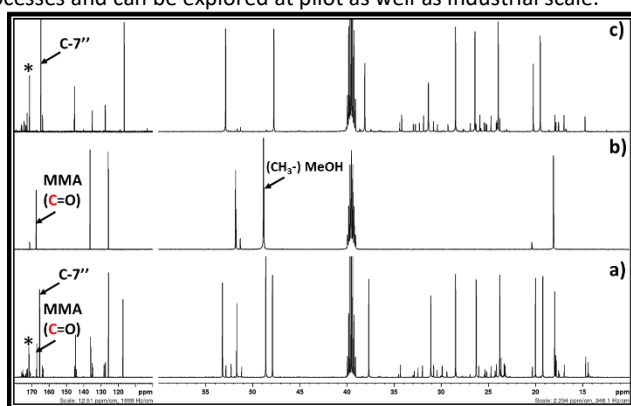

Figure 11. ^{13}C NMR spectra for the separation of MMA and methanol from [DBUH][methacrylate]. a) reaction mixture in MeOH: MMA and [DBUH][propionate], b) recovered MMA and MeOH from reaction mixture and, c) recovered [DBUH][methacrylate].

3.3 Synthesis of poly-MMA from recovered MMA

Considering the applicability of the MMA for the synthesis of poly-MMA, the free radical polymerization was proceed with recovered MMA (with MeOH) in the presence of benzoyl peroxide. As shown in Fig. 12, the ^{1}H NMR analysis represent the pure form of poly-MMA formed with 87% yield from the recovered MMA which was previously synthesized from SIL and methacrylic anhydride via release of molecular CO_2. The synthesis of poly-MMA from the recovered MMA was not optimized further as synthesis of polymeric compound was carried out to demonstrate the applicability of methanol as a signal solvent media for both MMA and poly-MMA synthesis.
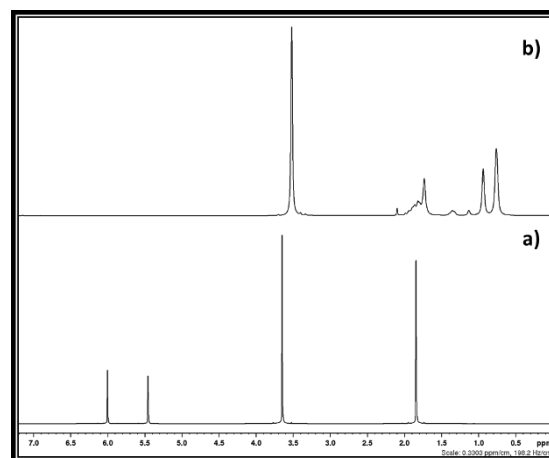

Figure 12. ^{13}C NMR spectra (in $CDCl_3$) for the synthesis of poly-MMA from MMA in methanol, a) MMA and, poly-MMA

Conclusions

In conclusion, in the present work, we successfully achieved the synthesis of acrylic plastic precursors namely methyl propionate and methyl methacrylate as well as poly-MMA in single solvent system such as methanol. The switchable ionic liquid obtained after chemisorption of molecular CO_2 by organic superbase DBU and methanol further reacted with either propionic or methacrylic anhydride and resulted to highly selective synthesis of methyl propionate or methyl methacrylate, respectively. This synthetic approach was fruitfully accomplished in both DMSO as well as methanol where the progress of reaction was not influenced by the choice of the solvent system. However, in contrast to DMSO as a solvent, methanol facilitated an efficient separation from the reaction mixture along with MP or MMA. High recovery level of alcoholic solutions of both esters were achieved and 85 and 92% yields of MP and MMA, respectively, were obtained. Further, the recovered MMA with methanol was polymerized to poly-MMA with 87% yield using free radical polymerization process. Hence, here methanol not only served as reagent and reaction media for CO_2 capture process but also assisted in the form of solvent in MP, MMA and poly-MMA synthesis. The 87 wt. % or 82 wt. % recovery of the comparatively expensive DBU was further also fruitfully achieved from [DBUH][propionate] or [DBUH][methacrylate], respectively, by using an alkaline NaCl saturated aqueous solution. Hence, in this report, highly selective, catalyst free, single solvent based, and hence economically favourable synthesis of both MP and MMA is represented. Being catalyst free, room temperature, cheaper and renewable solvent based process, this approach of acrylic plastic precursor synthesis can be explored at industrial level to tackle the drawbacks of currently ongoing industrial processes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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