Green Chemistry

Cutting-edge research for a greener sustainable future

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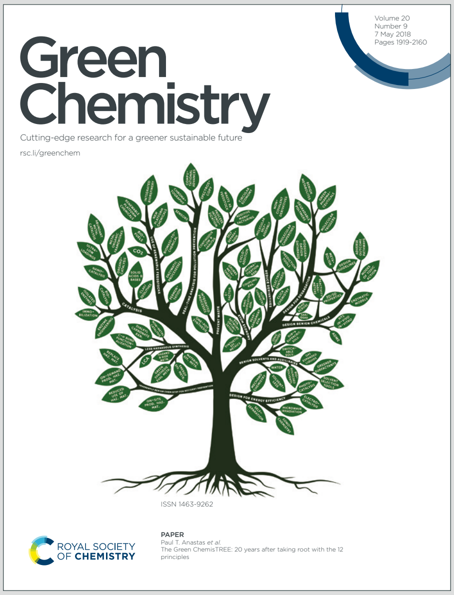

ROYAL SOCIETY OF CHEMISTRY

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Green Foundation box

1. **What advances in green chemistry have been discussed?**

To the best of our knowledge, this is the first comprehensive review focused specifically on organic carbonates as green media in laboratory organic syntheses up to industrial applications. As a result this work is based on an extensive bibliographic research covering the past 40 years.

2. **What makes the area of study of significant wider interest?**

The use of DACs as green solvents is appealing to a broad spectrum of scientific communities, industrial sectors, and policymakers committed to advancing sustainability, reducing environmental impact, and promoting safer chemical practices.

3. **What will the future of this field hold, and how will the insight in your review help shape green chemistry science?**

DACs offer more than just a replacement for toxic solvents; they present an opportunity to revolutionize various scientific fields towards more sustainable practices. The widespread adoption of DACs as green solvents is likely to have far-reaching effects, making them a valuable resource for researchers and industries focused on developing more sustainable processes.

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Organic carbonates as green media from laboratory syntheses to industrial applications

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The research for greener solvents is of paramount importance when aiming to a sustainable process. In order to be able to replace traditional hazardous media, green solvents must display negligible environmental effects, biological degradability while at the same time being available in large scale and exhibit comparable or even superior performances compared to currently employed media. In this scenario, organic carbonates (OCs) are among the most prominent since they are commercially available at good price, and they also offer a broad range of tunable proprieties that render them usable for a wide range of applications. From these premises, the herein proposed review focuses on OCs used as green media from laboratory synthetic approaches to industrial applications. According to our literature screening that covered the last 40 years, organic carbonates are mostly investigated as electrolyte solvents (23%), media in organic synthesis (21%) and as solvents for extraction of compounds from different biological and non-biological matrices (13%). Nevertheless, OCs have found applications in several other fields spanning from analytical chemistry to the biological/biochemical area up to the restoration of ancient manufacts. Most of the OCs used in these applications are dialkyl carbonates (DACs) commercially available at cheap prices, i.e., dimethyl carbonate (DMC), propylene carbonate (PC) and ethylene carbonate (EC). However, thanks to simple procedures, new custom-made organic carbonates have been synthetized and used for membrane casting, for polymers and plasticizers preparations, surface modifications of materials and as electrolytes in Li-ion batteries. Organic carbonates go beyond simply replacing toxic solvents; they offer an opportunity to transform a varierty of processes into sustainable practices. From enhancing battery performance and advancing materials science to driving innovations in green chemistry and improving industrial sustainability, their potential is vast. The adoption of organic carbonates as green media is likely to have far-reaching effects, making them a valuable tool for researchers and industries aiming to develop more sustainable processes.

1. Introduction

Following the worldwide increase in environmental awareness, also highlighted in the recent European Green Deal (EGD),[1,2] traditional chemical methods are being replaced with new and more sustainable ones. This of course includes first and foremost the selection and use of solvents. In fact, solvents are responsible for the consumption of more than 60% of the energy required in an industrial plant and they are the most discarded substances in industrial processes, rendering them one of the major responsible for environmental damage.[3–6] Solvent selection is crucial as it impacts the plant economics and operation time of the production process.[7]

On this topic, several pharmaceutical companies, i.e., Pfizer, GSK, Astra Zeneca and Sanofi, have combined the major solvent selection guides so far developed.[8,9] The criteria considered were safety (S), occupational health (H), environment (E), quality (risk of impurities in the drug substance), industrial constraints (i.e., boiling point, freezing temperature, density, recyclability) and cost.[9,10] The result uses a “traffic light” colour code system: green for preferred solvents, yellow for compounds showing some health or environmental issues and red for toxic solvents which need to be substituted. A high number of commercially available solvents commonly used in organic synthesis are evidently not recommended due to their high volatility, flammability, hazardousness and many other health risks.

In this view, it is necessary to explore more environmentally friendly and tunable solvents, which have a negligible environmental effect, are biologically degradable[3,11] and can replace traditional hazardous media in chemical processes. Solvents fulfilling these requirements are called “green” solvents.[3,6,12] A green solvent must possess most of the following characteristics: low vapor pressure, high boiling point, low price, recyclability, non-toxicity, chemical and thermal stability and non-flammability while possibly being a bio-derived product.[13–15] In addition, a green solvent should be available in large scale, thus ensuring a stable market production. It must be prepared through energy-saving processes with high atom economy synthetic procedures and should demonstrate comparable or even superior performances compared to currently used solvents.[15] A wide-range of green solvents derived from renewable feedstocks are currently accessible; (bio)ethanol, ethyl lactate, 2-methyl-

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Supplementary Information available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x tetrahydrofuran (2-Me-THF), cyclopentyl methyl ether (CPME), glycerol, dimethyl isosorbide (DMI), γ-valerolactone (GVL) and Cyrene are some of the most common examples which can be also defined as bio-derived solvents. Furthermore, other types of compounds are also commonly employed as green solvents, i.e., organic carbonates (OCs), CO_2 and supercritical CO_2 ($scCO_2$), ionic liquids (ILs) derived from amino acids, proteins, lignin and polysaccharides,[16] deep eutectic solvents (DES) and natural DES.[17–19]

Among them, this review will focus on OCs, exploring their use as media in different fields.

These compounds offer a broad range of proprieties, tunable according to their chemical structures. In literature, numerous organic carbonates, both commercially available and custom-made, have been employed in various fields as illustrated in Figure 1 (OCs applications) and Figure 2 (most used OCs). According to our extensive literature screening covering the last 40 years, OCs have been mostly investigated as electrolyte solvents, media in organic synthesis and for the extraction of compounds from different biological and non-biological matrices.

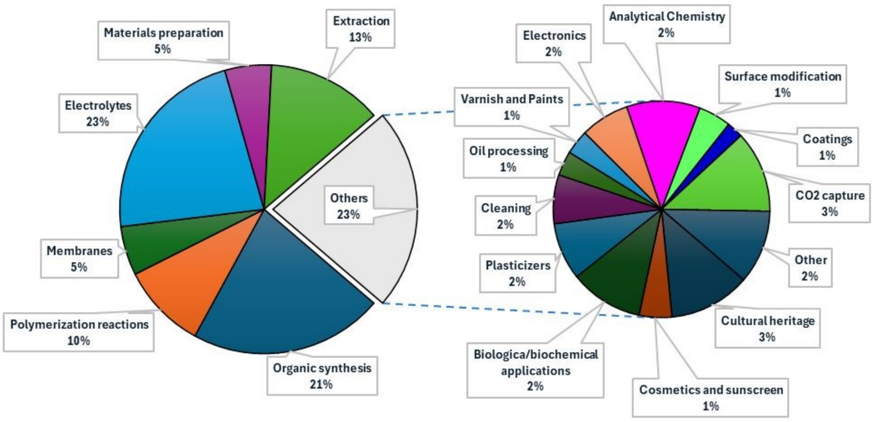


Figure 1. Literature screening on the applications of OCs as solvents. The bibliographic search was conducted exploiting the Reaxys database choosing years from 1980 up to July 2024, with selected keywords: "solvent" and "carbonate" combined with the OC chemical structure considering any side chain group and ring-closure. From this screening, 2761 articles and patents were obtained from which were excluded works where OCs were used as reagents or as solvents and reagents.

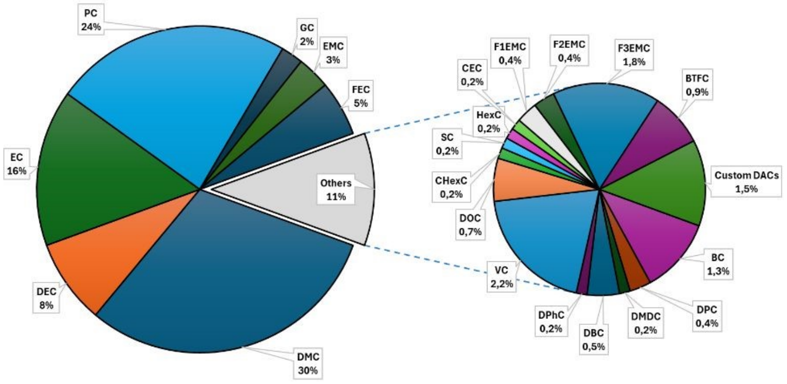
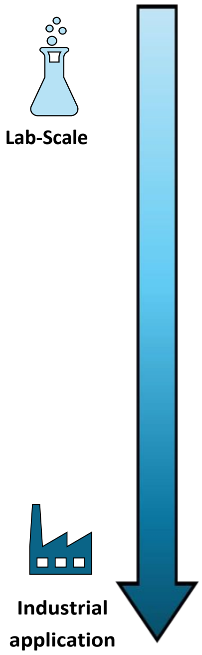


Figure 2. Literature screening on the OCs used as solvents. The bibliographic search was conducted exploiting the Reaxys database choosing years from 1980 up to July 2024, with selected keywords: "solvent" and "carbonate" combined with the OC chemical structure considering any side chain group and ring-closure. From this screening, 2761 articles were obtained from which were excluded works where OCs were used as reagents or as solvents and reagents.

Nevertheless, OCs have found applications in several other fields ranging from analytical chemistry, principally as mobile phases for products separation and identification, to the biological/biochemical area and for the restoration of ancient manufacts (Figure 1). Most of the OCs used are dialkyl carbonates (DACs) and can be easily purchased on the market at cheap price, i.e., dimethyl carbonate (DMC), diethyl carbonate (DEC), propylene carbonate (PC) and ethylene carbonate (EC) (Figure 2). It must be mentioned that PC and EC are well-known electrolytes solvents, which represents the most studied application area for OCs (Figure 1). Despite this predominance, custom-made OCs have also been employed in different areas to meet polarity or solubility criteria required for specific applications (Figure 2).

From these premises, the present work aims to give an overview focused exclusively on the applications of OCs as solvents, highlighting their use in lab-scale chemical transformations, in large scale industrial processes as well as in end-of-use products. Numerous reviews have been published on OCs as green reagents. However, to the best of our knowledge, this is the first comprehensive review focused solely on their use as green media.

In particular, the rationale of this work has been organized as follows:



- After illustrating the chemical properties of the most studied OCs, the review discusses extensively the lab-scale chemical transformations where these compounds are used either as the sole medium or as co-solvents (Section 4);
- The second part of the review is dedicated to processes that can be considered in between lab- and industrial-scale i.e., (co-)polymerization and depolymerization reactions, fabrication of adhesives and CO_2 capture procedures (Sections 5-6);
- The third part is dedicated to the application of OCs in industrial processes such as for the preparation of membrane, fibres, films fabrication, materials and nanoparticles preparation, extraction processes, as electrolytes in batteries, etc. (Sections 7-21).

2. Properties and stability of organic carbonates

OCs display completely different proprieties depending on their chemical structure. The characteristics of the most studied OCs (Figure 1-2) – DMC, DEC, EC and PC – together with some of the most employed traditional toxic media (see also Table 2) are reported in Table 1.

Cyclic OCs generally display a higher dipole moment and dielectric constant compared to the linear ones. For this reason, PC in particular is well-suited for anhydrous electrochemical applications.[20,21] Moreover, the polarity and hydrogen-bond acceptor properties (basicity, β) of PC (0.39) match perfectly those of acetonitrile (0.38).[22] Linear DACs like DMC and DEC, although displaying similar basicity, possess lower polarities which resemble methylene chloride and THF.[23–26] Only scant data are available for other organic carbonates even if modelling predictions of those parameters may be a powerful tool to overcome this limitation.[27–31]

Concerning OCs solubility, most of them show only limited or no miscibility with water,[32,33] despite displaying characteristics of highly dipolar solvents similarly to other compounds like dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF).[33] In a recent study, it was demonstrated that the substitution of hydrocarbon chains with more polar glycol-based moieties led to a drastic increase of OCs water solubility.[34,35] Thus, the tuning of OCs side chains may allow a wider application of these compounds both as solvents and reagents.[35,36]

OCs can be considered chemically stable under normal conditions. However, at elevated temperature these compounds can decompose releasing mainly CO_2. In particular, DMC can release CO_2 and dimethyl ether at T>150 °C in an inert atmosphere, while methanol can originate from DMC hydrolysis in the presence of water.[49] Similarly, DEC can decompose into ethylene, ethanol and CO_2.[49] Also longer chain DACs have been shown to decarboxylate in the presence of hydrotalcites, producing the corresponding ethers.[50] In general, linear OCs degrade at lower temperatures than cyclic ones, i.e., EC degrades at 335 °C meanwhile PC at 316 °C.[49]

It should be mentioned that the reactivity of DMC and its derivatives were thoroughly investigated by the work of Tundo et al., from which it is evident that these compounds can easily react with a variety of nucleophiles yielding either the corresponding alkoxycarbonylated or alkylated derivatives according to the reaction conditions.[51]

Table 1. Chemical-physical proprieties of the most investigated organic carbonates compared to some of the most employed toxic solvents.

	DMC	**DEC**	**EC**	**PC**	**CH_2Cl_2**	**CH_3CN**	**Toluene**	**DMF**
Molecular weight (g/mol)	90.08	118.13	88.06	102.09	84.93	41.05	92.14	73.09
Melting point (°C)	4.6[37]	−43[37]	34-37[38]	−48.8[3]	-97[a]	-48[a]	-93[a]	-61[a]
Boiling point (°C)	90.3[37]	126[37]	248[39]	240[3]	40[a]	81[a]	110[a]	153[a]
Density (g/cm³)	1.069[37]	0.975[37]	1.321[40]	1.201[3]	1.325[a]	0.786[a]	0.865[a]	0.944[a]
Water solubility (g/L)	139[37]	Insoluble[37]	778[34]	200[34]	0.013[b]	>800[b]	0.53[b]	1000[b]
Dielectric constant (ε)	3.20[41]	2.82[42]	89.78[43]	66.6[44]	8.93[c]	37.5[c]	2.38[c]	36.7[c]
Dipole moment (μ, D)	0.91[45]	1.07[46]	4.81[43]	5.36[44]	1.55[c]	3.45[c]	0.43[c]	3.86[c]
Explosion limit[a]								
LEL (% V)	4.2	1.4	3.6	1.8	13.0	4.4	1.2	2.2
UEL (% V)	12.9	11.0	16.1	14.3	22.0	16.0	7.1	16.0
Flash point[a] closed cup (°C)	16.0	25.0	143	132	Does not flash	2.0	4.4	57.5
Ignition temperature[a] (°C)	n.r.	445	n.r.	n.r.	605	n.r.	n.r.	435
Vapour pressure[a] (hPa at 20.0-25.0 °C)	24	13	<1	0.06	584	98.64	30.88	3.77
Solvent polarity (E_T(30), kcal/mol)	41.1[47]	36.2[47]	48.6[48]	46.6[47]	40.7[47]	45.6[47]	33.9[47]	43.2[47]

LEL: lower explosive limit; UEL: upper explosive limit; n.r.: information not reported, V = volume ; [a]values available on Sigma-Merck safety data sheet (SDS) of the corresponding compound; [b]values available on https://pubchem.ncbi.nlm.nih.gov/; [c]values available on https://depts.washington.edu/eooptic/linkfiles/dielectric_chart%5B1%5D.pdf.

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OCs proprieties of ambident electrophiles may therefore hamper their applications as media, with possible side reaction occurring due to their reactivity. Similarly, cyclic OCs may undergo ring opening in the presence of a suitable nucleophile, thus leading to side products formation. Some examples about these issues are reported throughout Section 4.

3. Global market, production costs and safety aspects of organic carbonates

3.1 Global market production of the principal organic carbonates

According to ChemAnalyst and KBV reports, the global EC production was estimated between *ca* 320 000 and 460 000 tonnes in 2022 with a projection to reach 865 000 tonnes by 2032 (compound annual growth rate – CAGR - of 6.5% from 2023 to 2032).[52,53] Different reports forecasted the global EC market size to reach a value between 970.4 million USD and 1.16 billion USD by 2030, with a CAGR from 8.6% to 13.7% during the forecast period.[53,54]

The global market of PC was of approximately 470 000 t/year in 2022, and it is anticipated to grow at a CAGR of 5.6% until 2032, reaching 800 000 t/year (Chemanalyst report). The increasing demand for electric vehicles and portable electronic devices is also driving the PC market, together with its utilization in skin care formulations products, coatings, paints, sealants, adhesives and degreasers.[55,56]

According to a report by Grand View Research, the global PC market was valued at approximately 393.1 million USD in 2023 and is projected to reach 610.9 million USD by 2030.[56]

The global DMC production is the highest among the commercially available OCs, with a value estimated around 926 000 tonnes in 2022 with an expected CAGR of 5.4% until 2032,[57] with its major application being in polycarbonate production.[58]

The DMC market was instead valued between 1.10 and 1.17 billion USD in 2023 and is projected to reach 1.9 billion USD by 2028.[59]

3.2 Techno-economic analyses of organic carbonates production

One of the most used processes for DMC production, patented by Asahi Kasei in 2006, involves the CO_2 insertion into epoxides, with the formation of EC or PC as intermediates. These are then converted into DMC via a transesterification reaction with methanol.[60,61] Other well-known procedures for DMC production rely on the oxidative carbonylation of methanol (EniChem, Bayer and UBE processes)[62–65] and on the alcoholysis of urea.[66,67]

On this aspect, various techno-economic assessments were performed during the years to evaluate the economic feasibility of DMC production through different routes, mainly involving CO_2 as starting reagent.[68–70] Considering the oxidative carbonylation of methanol and the direct urea methanolysis as synthetic methods, the steps of methanol and urea syntheses appear to be the major capital investment contributors, rather than the DMC synthesis step.[70] In this scenario, the DMC production cost was calculated to be around 520 €/t.[68]

The Asahi Kasei route was found to give the best performance in terms of energy consumption (11.4% improvement), net CO_2 emission (13.4% improvement), in global warming potential (58.6% improvement) and in human toxicity-carcinogenic (99.9% improvement) compared to the Bayer process.[69] It is worth mentioning that in the process forming EC as intermediate to DMC, high purity ethylene glycol (EG) is also produced as by-product.[69] EG can then be employed in other numerous industrial processes, such as in the synthesis of polyethylene terephthalate (PET) and polyethylene furanoate (PEF) as well as for energy, automobiles, and chemical applications.[71]

In addition, a techno-economic assessment performed by Kontou and co-workers in 2022, analysed the DMC/CO_2 ratio of different DMC production concepts based on the initial formation of EC from the reaction of ethylene oxide (EO) with CO_2 followed by its subsequent transesterification with methanol to produce DMC and EG as side product.[72]

Syntheses carried out with fossil-derived methanol from the market and CO_2 procured from a pipeline network were compared to those in which MeOH was produced on-site using externally procured green hydrogen and CO_2 was captured from a coal-fired power plant. The DMC/CO_2 ratio of the considered scenarios ranged from 1.38 kg/kg to 0.53 kg/kg which can be further lowered to negative CO_2 emission values (−105.48 kt/a) when grid electricity and natural gas are used for covering the electricity and heating needs of the plant.[72]

From these evaluations, the DMC minimum selling price of the different scenarios ranged from 634 to 1263 €/t, which could be reduced (659-707 €/t) assuming a future decrease of the green hydrogen price. In this case DMC minimum selling prices would range between 659 and 707 €/t, which are below the current market price of 849 €/t.[72]

Concerning the other most used cyclic OCs, i.e., EC and PC, they can be obtained using the same procedures previously described for the synthesis of DMC, as they are formed as intermediates from the reaction of CO_2 with the corresponding epoxide (namely, EO and propylene oxide - PO). For this reason, it is safe to assume that their production cost and CO_2 emissions would be lower compared to DMC.

Despite this consideration, other studies focused on the techno-economic analysis of alternative EC and PC syntheses, either

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starting from EG instead of the petroleum-derived EO[73] or from CO_2 and PO in the presence of different ILs as catalysts (namely, [P66614][Br] and 1-n-ethyl-3-methylimidazolium chloride), respectively.[74,75] In the case of PC synthesis, the optimal configuration for the former system displayed an energy consumption of approximately 0.6 kWh/kg_{PC} and utility costs of 6.6 USD/t_{PC}.[74] For the latter one instead, the net cost of duty was calculated to be 4.26 USD/t_{PC} considering a production of 91 000 t/year of PC by using 4.5 t/ hr of CO_2.[75]

For EC production instead, none of the cases tested showed to be feasible for commercialization at an annual EC production of 5 ktonnes. The minimum selling price of EC would range between 6.44 USD/kg and 16.73 USD/kg against a current market price fluctuating between 0.88 and 1.16 USD/kg.[73,76]

Data about market production and costs of other more complex organic carbonates are still lacking. However, various processes for the synthesis of linear organic carbonates rely on the use of DMC as starting reagent which is then subjected to a transesterification in the presence of the desired alcohol.[34,77] Custom made cyclic OCs reported in this review were instead synthesized either by reacting GC with the corresponding acyl chloride[78] or by reacting a suitable triol with urea in the presence of a catalyst.[79]

3.3 Safety aspects of organic carbonates

Organic carbonates are generally considered as non-toxic compounds, with most of the toxicological studies performed on DMC. DEC is instead listed as "an experimental tumorigen and teratogen" and "mildly toxic by subcutaneous route". Specific toxicity data obtained through animal testing were collected by Pacheco and co-workers.[80]

A safety assessment regarding DACs used in cosmetics - namely, dicaprylyl carbonate, bis-propylheptyl carbonate, C_{14}-C_{15} dialkyl carbonate, diethylhexyl carbonate, DMC and DPC - was published by The Cosmetic Ingredient Review (CIR) Expert Panel established with the support of the U.S. Food and Drug Administration (FDA) and the Consumer Federation of America.[81,82] The report presented an overview of use, toxicokinetic and toxicological effects of the studied DACs with experiments conducted on rats, cavies and human skin samples concluding that the studied DACs "are safe in the present practices of use and concentration […] when formulated to be non-irritating."[81]

The Environmental Protection Agency (EPA) indicated PC as a low concern chemical based on experimental and modelled data.[83]Acute toxicity tests were performed by dermally administering PC to rats and rabbits at 5000 mg/kg-bw and 3000 mg/kg-bw, respectively and no mortality was seen after 14 days (LD_{50} > 5000 and LD_{50}>3000, respectively). Rats were also exposed to PC aerosol via inhalation at 0.1, 0.5 and 1.0 mg/L for 6 hours/day, 5 days/week, for 14 weeks. Ocular irritation and periocular swelling were seen at 0.5 and 1.0 mg/L. On the other hand, rats exposed to PC did not develop any chromosomal aberrations after intraperitoneal injection of PC at 1666 mg/kg-bw.[84]

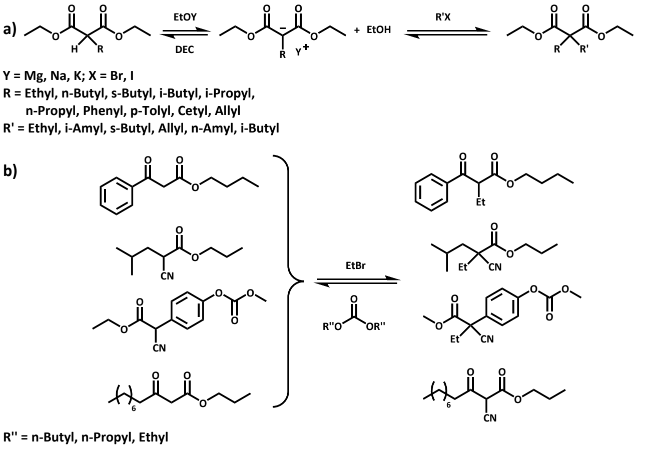
In addition, cytotoxicity tests were conducted via colorimetric MTT assay on a selection of custom-made alkyl methyl carbonates and 2-(2-methoxyethoxy) carbonates $(DGly)_2C$ and DGlyMC. None of them showed any cytotoxicity effect at all tested concentrations, both after 24 h and 48 h after the treatment of the cells. Moreover, computational analyses involving different software (CASE Ultra by MultiCASE Inc., USA; Model Applier by Leadscope, USA) and models based on quantitative structure-activity relationships (QSAR) predicted all DACs tested to be not mutagenic in compliance with ICH guideline M7.[34,85]

4. Organic carbonates as media in organic syntheses

OCs have been broadly investigated as green reaction media for many chemical transformations. In 1942, Wallingfod, Thorpe and Homeyer firstly reported DACs as solvents in the alkylation of malonic esters, β-keto esters and α-cyano esters (Scheme 1).[86] They discovered that, using DACs as media, the formation of the sodium derivative of these substrates went to completion and cleavage by alcoholysis was avoided. Several malonic esters, not achievable by usual methods, were prepared operating in DEC solution. For instance, alkyl chains like Et, Bu, iso-amil, n-amyl, allyl, benzyl, sec-butyl, etc., were introduced with yields ranging from 70 to 95% (Scheme 1).[86]

Since the 1960s applications of OCs as solvents have spread to nearly every field of chemistry.[33] Moreover, cyclic carbonates, especially EC and PC, are well known for their high solvency.[87] Thus, organic cyclic and linear carbonates started gaining attention as they might partially or totally replace more expensive or more toxic solvents such as N-methyl pyrrolidone (NMP), dichloromethane, DMF, isophorone, etc.[33] in various synthetic approaches (Table 2, Figure 3).

Linear and cyclic carbonates have been widely used as green solvents due to their non-hazardousness, in substitution of more toxic and fossil-derived compounds normally used in different organic synthesis processes.



Scheme 1. a) First examples of organic carbonate as reaction media – alkylation of malonic esters in DEC; b) alkylation of β-cheto and α-cyano esters in organic carbonates.[86]

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Table 2. OCs employed as green solvents in organic synthesis in substitution of toxic or hazardous solvents.

General application	Specific application	Organic carbonate solvents	Toxic solvents	Literature
Simple chemical reactions	Etherification	PC	CH_2Cl_2, CH_3CN, benzene, toluene	89,92
	Esterification	DMC	n.r.	88
	Chlorination and bromination	DMC, PC, DEC	$CHCl_3$, chlorobenzene, CCl_4	90,91
	Oxidation and epoxidation	DMC, DEC, PC, DPC, BC	CH_3CN, ionic liquids, DMF, NMF, NMP, DMA, THF	93–103,104,105
	Amine synthesis	DMC, PC	$CHCl_3$, Toluene	106–108
	Amide synthesis	DMC	CH_2Cl_2	109
	Wolff rearrangement/acylation	DMC, DEC	DMF, CH_3CN, toluene, DMSO, DCE	110
	Dehydration	DMC	THF	111–117
Rh-catalysed reactions	Hydroformylation	DMC, DEC, PC	Toluene, benzene	118–121
	Co-oligomerization	PC	n.r.	118
	Ortho-diarylation	DEC	NMP, 1,4-dioxane	122
	Hydroacylation	PC	DCE	123
Pd-catalysed reactions	Asymmetric allylic substitution	PC, BC, DEC	CH_2Cl_2	124
	Telomerization	DMC, DEC, EC, PC, BC, GCP, GCB	CH_3CN	78
	Allylation of heteroarenes	DMC	DMF, 1,4-dioxane, CH_3CN	125
	Synthesis of lactones	DMC	Toluene, CH_2Cl_2	126
	Hydrogenation	DMC	n-heptane	127
	Phenoxycarbonylation of aryl iodides	PC, EC	DMF, 1,4-dioxane	128
	Coupling	DMC, DEC, EC, PC, GC	THF, toluene, anisole, 1,4 dioxane, DMA, DMF	129–135
	Synthesis of oxime ether derivatives	DMC	n.r.	136
Ni-catalysed reactions	Hydrodeacetoxylation	DMC	Toluene	137
Pt-catalysed reactions	Hydrosilylation	PC	Toluene, cyclohexane	138,139
Ru-catalysed reactions	Olefin metathesis	DMC, PC	Benzene, toluene, CH_2Cl_2, chlorobenzene	140–143
Other applications as media in organic synthesis	Organic carbonates and ionic liquids as media in organic synthesis	DEC, PC	n.r.	144–146
	Phase transfer catalysis	DMC	Toluene, chlorobenzene	147
	Enantioselective reactions	PC, EC	DMF, CH_2Cl_2	148–152
	Photocatalytic reactions	DMC	Toluene, CH_3CN, BTF, DMF, benzonitrile, propionitrile, butyronitrile	153–159
Other reactions	Condensation/rehydration	DMC	cyclohexane	160
	Radziszewski reaction	PC	DMSO, DMF	161
	Synthesis of cyclodextrin-based supramolecular assemblies	DEC	n.r.	162
	Complexation	PC	DMF	163
	Claisen rearrangement	PC	DCB	164
	Ring opening	DMC	CH_2Cl_2, Et_2O, CH_3CN	165

n.r.: information not reported; DMA: dimethyl acetamide, GPC: glycerol carbonate propionate, GCB: glycerol carbonate butyrate, GC: glycerol carbonate, DPC: dipropyl carbonate, BC: butylene carbonate, Gly_2C: bis(2-methoxyethyl) carbonate, GlyMC: 2-methoxyethyl methyl carbonate, DGlyMC: 2-(2-methoxyethoxy)ethyl methyl carbonate, $DGly_2C$: bis(2-(2-methoxyethoxy)ethyl) carbonate, DPhC: diphenyl carbonate, EMC: ethyl methyl carbonate, DAllC: diallyl carbonate.

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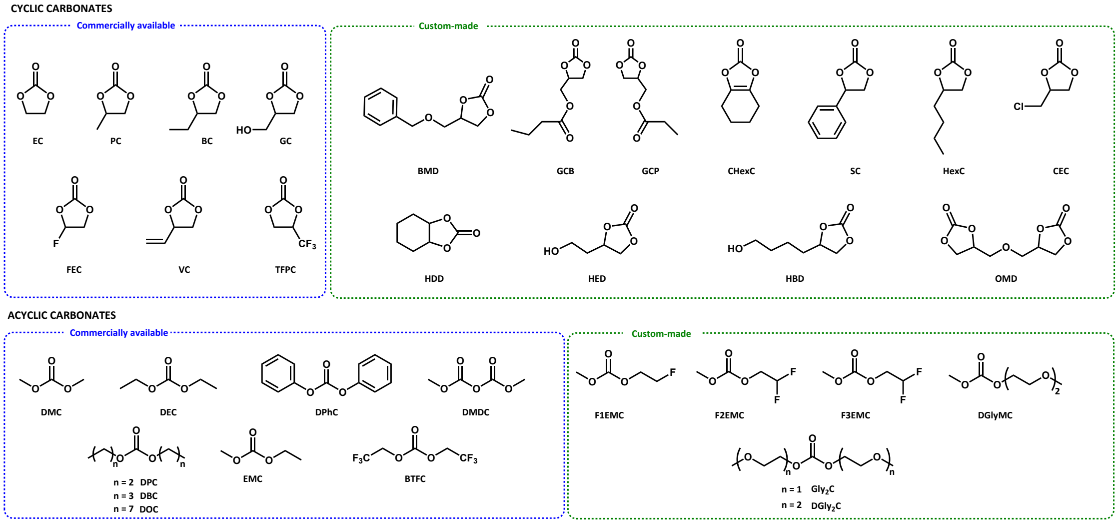


Figure 3. Chemical structures of cyclic and acyclic organic carbonates that have found applications as reaction media.

In many cases, OCs have shown to be viable alternative solvents, able to compete and in some cases even outperform traditional solvents. In the following sections are reported some of the most prominent works where cyclic and linear OCs were used as solvents in different organic synthesis reactions as summarized in Table 2.

4.1 Etherification and Esterification reactions

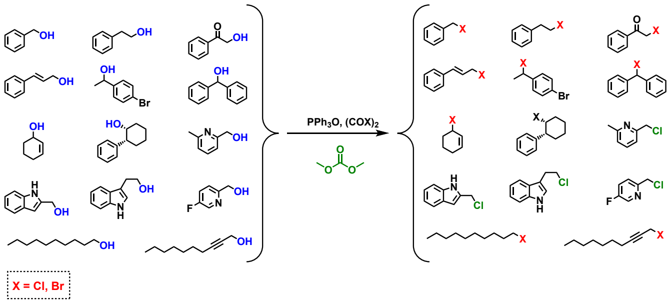
To the best of our knowledge only one example was reported in literature where OCs were employed as solvents in esterification reactions. In this study the synthesis of lipophilic esters of tyrosol, homovanillyl alcohol and hydroxytyrosol were performed in DMC. The reactions were carried out at room temperature in the presence of the selected C2–C18 acyl chloride added in a slight excess. The final products were isolated in yields ranging from 90 to 98% in the case of tyrosyl and homovanillyl-derived esters, while yields spanned from 60 to 68% for hydroxytyrosyl esters.[88]

Similarly, only scant works focus on the application of OCs as solvents in etherification reactions. In particular, symmetrical and non-symmetrical etherification of benzyl alcohols were performed in PC in substitution of CH_2Cl_2 and CH_3CN. The symmetrical etherification reaction was carried out in the presence of $FeCl_3{\cdot}6H_2O$ (5 mol %) as the catalyst and led to the corresponding symmetrical ethers in 53 to 91% yields.Recently, DMC was employed in substitution of benzene and toluene in the self-etherification of the bio-based platform chemical 5-hydroxymethyl furfural (HMF) to obtain 5,5'-[oxybis(methylene)]bis-2-furfural (OBMF). The reaction was carried out in the presence of a heterogeneous Lewis acidic catalyst, $Fe_2(SO_4)_3$ allowing the recovery of OBMF in *ca* 80% yield.[89]

4.2 Chlorination and bromination

Appel chlorination and bromination mediated by triphenylphosphine oxide (PPh_3O) was performed using DMC as solvent instead of chloroform (Scheme 2).[90] The Appel reaction allows the conversion of alcohols to the respective activated alkyl halide promoted by PPh_3O. Triphenylphosphine oxide is converted to its respective chlorophosphonium salt (CPS) by reaction with oxalyl chloride $(COCl)_2$. Finally, CPS reacts with an alcohol leading to the corresponding alkyl chloride.[90]

The substitution of DMC with chloroform led to a slightly longer reaction time (15 min instead of 5 min) to achieve the total conversion of benzyl alcohol into its chloride. This suggests that the generation of CPS in DMC is a slower process than in chloroform. In addition, CPS needed a higher amount of DMC to be completely dissolved.[90] Isolated yield values for the chlorination and bromination reactions of different alcohols in DMC varied between 21 and 83% in the former case and from 43 to 89% in the latter one.[90]



Scheme 2. Appel chlorination and bromination reactions of different alcohols in DMC.[90]

Another example is the Wohl–Ziegler bromination of 2-cyano-4'-methylbiphenyl conducted in PC (conversion and yield of 83% and 76%, respectively) and DEC (conversion and yield of 89% and 71%, respectively) in substitution of commonly employed chlorinated solvents such as chlorobenzene or carbon tetrachloride. The obtained product, 4'-(bromomethyl)-2-cyanobiphenyl (BCB) is a key building block to various sartans, valuable nonpeptide angiotensin II antagonists (Scheme 3).[91]

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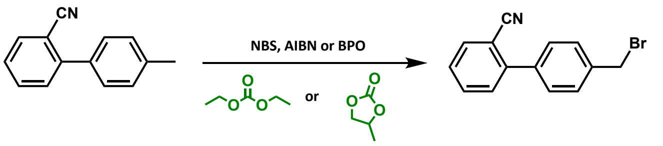
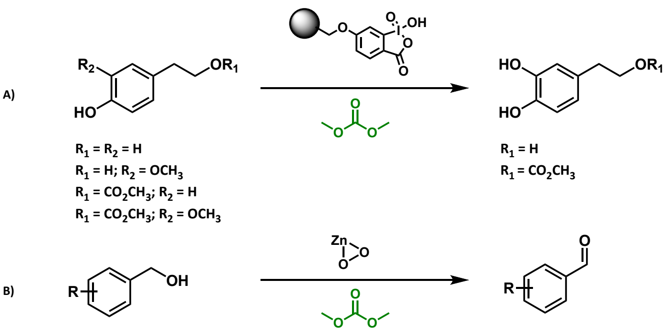


Scheme 3. Bromination of 2-cyano-4′-methylbiphenyl using N-bromosuccinimide (NBS) to yield 4′-(bromomethyl)-2-cyanobiphenyl (BCB).[91]

4.3 Oxidation reactions

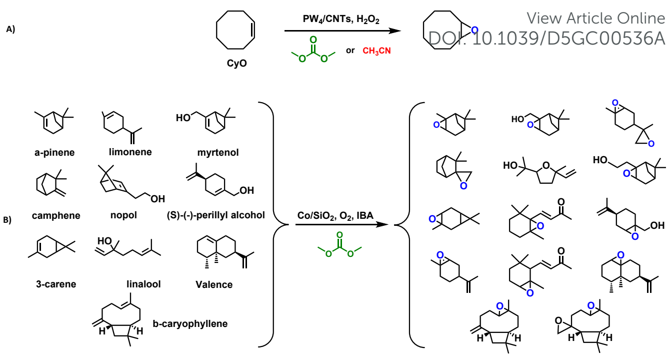
DACs were investigated as green alternative solvents for the oxidation of aryl–alkyl ketones[102] and various aromatic compounds, i.e., styrene, naphthalene derivatives, sulfides, alcohols and phenolic molecules in the presence of different catalysts.[94,97,98] Bernini and co-workers relied on a H_2O_2/methyltrioxorhenium ($MeReO_3$, MTO) catalytic system using DMC as media. The studied oxidations proceeded with good conversions (>98% via GC-MS) and with yields up to 98%.[93]

DMC showed good performances as green media for chemoselective and regioselective oxidation and demethylation of phenolic compounds in the presence of polymer-supported 2-Iodoxybenzoic acid (IBX), to obtain bioactive catechol derivatives (Scheme 4A).[94,97] DMC was also applied for the oxidation of aromatic alcohols to the corresponding carbonyl compounds employing zinc peroxide (ZnO_2) nanoparticles (Scheme 4B; yields varying from 79 to 98%).[98]



Scheme 4. A) Chemoselective and regioselective oxidation of phenolic compounds in the presence of polymer-supported IBX[94]; B) oxidation of aromatic alcohols to the corresponding carbonyl compounds in DMC.[98]

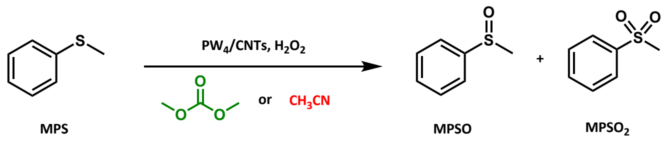
DMC was utilized as a solvent for the epoxidation of alkenes (Scheme 5) in substitution of the commonly employed acetonitrile. Reactions were performed in the presence of different heterogeneous catalysts, i.e, $[PO_4\{WO(O_2)_2\}_4]$ (PW_4), nitrogen-free or nitrogen-doped carbon nanotubes (CNTs or N-CNTs)[103] and silica-supported cobalt-based (Co/SiO_2) materials.[95]



Scheme 5. A) Cyclooctene (CyO) epoxidation with H_2O_2 in DMC; B) Epoxidation of bio-renewable terpenes in DMC.[95]

In particular, cyclooctene (CyO) epoxidation with H_2O_2 in DMC showed better performances in the presence of PW_4/CNTs and a tetrahexylammonium salt of PW_4 (THA-PW_4) as catalysts (conversion: 93% and 80%, respectively; epoxide selectivity: 97% and 100%, respectively) compared to when PW_4/N-CNTs was employed (conversion: 37%; epoxide selectivity: 89%) despite similar initial reaction rates (Scheme 5A).[103] Encouraging results were also achieved for the epoxidation of a series of bio-renewable terpenes in DMC, i.e., β-pinene, camphene, 3-carene, limonene, valencene and β-caryophyllene (yield varying between 46 and 99%) as well as terpenes containing an alcohol functionality, i.e., myrtenol, nopol, (S)-(-)-perillyl alcohol and linalool (yield varying between 45 and 92%) using molecular oxygen, isobutyraldehyde (IBA) as a sacrificial reductant and a Co/SiO_2 catalyst (Scheme 5B).[95]

In addition, the catalytic performance of PW_4/CNTs catalysts was assessed in the selective oxidation of organic sulfides with H_2O_2 using methyl phenyl sulfide (MPS) as a model substrate (Scheme 6) and compared with that of homogeneous PW_4. In this case, reactions carried out in acetonitrile in the presence of homogeneous THA-PW_4 showed a higher sulfide conversion (93 %) and selectivity to sulfoxide (83%) compared to when DMC was employed (86 and 70%, respectively).[103]



Scheme 6. Oxidation of organic sulfides in DMC and acetonitrile as media in the presence of H_2O_2 and PW_4/CNTs as catalyst. [103]

Synthetic protocols for the synthesis of guanidines and amides using DMC as green media were reported in Baeten and Ramarao works, respectively. Particularly, guanidines can be obtained via oxidative rearrangement of amidines into carbodiimides, followed by an *in-situ* reaction with amines (Scheme 7A).[105] Amides can be isolated from the corresponding imines by using molecular oxygen in air as the sole oxidant (Scheme 7B).[104]

PC was found to significantly enhance the oxidation reaction of cyclohexane over Au/SiO_2 catalyst with 22% conversion and 83% selectivity towards the mixture cyclohexanone/cyclohexanol (K/A-oil; 65% and 18%,

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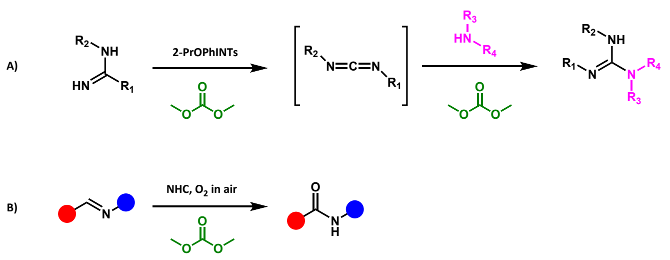
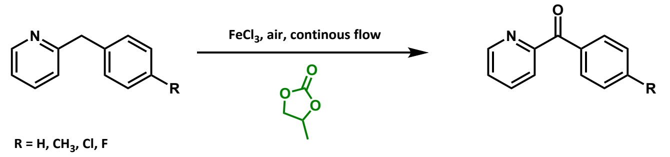
respectively), that can be used for the production of Nylon-6 and Nylon-6,6.[99] Cyclic carbonates conversions (from 18% to 22%) and selectivities (about 81%) towards the K/A-oil are much higher than linear organic carbonates, i.e., DMC, DEC, DPC, EC and BC (conversions between 3% and 5%; selectivities between 44% and 56%).[99]



Scheme 7. DMC as solvent for the A) synthesis of guanidines from amidines and B) synthesis of amides from imines. NHC: N-Heterocyclic Carbene [104, 105]

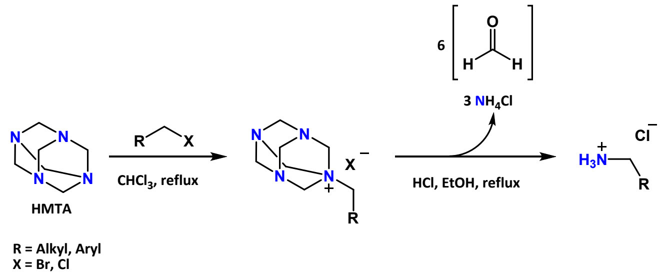
Another relevant example is the iron-catalysed aerobic oxidation of 2-benzylpyridines to their corresponding ketones that was performed in continuous flow using PC in substitution of more toxic dipolar aprotic solvents i.e., CH_3CN, DMF, NMF, NMP, DMA and DMSO (Scheme 8).[100] The reaction time was significantly reduced from hours to minutes and molecular oxygen was replaced by synthetic air as oxygen source.[100]



Scheme 8. Iron-catalysed aerobic oxidation of 2-benzylpyridines in continuous flow using PC as solvent. [100]

4.4 Synthesis of amines and amides

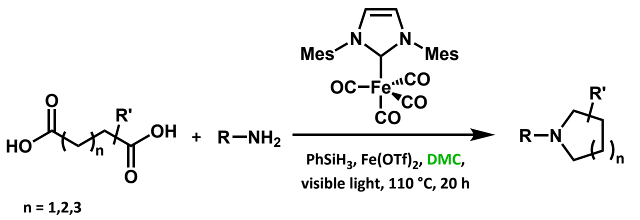
DACs demonstrated to be suitable reaction media for the synthesis of both linear and cyclic amines. As an example, primary amines were obtained via the Delépine reaction[166] (Scheme 9) by reacting hexamethylenetetramine (HMTA) with an alkyl or benzyl halide in the presence of DMC instead of the commonly employed solvent $CHCl_3$. The product was obtained with comparable yield values.[106]



Scheme 9. Synthesis of primary amines via Delépine Reaction. [106]

Moreover, DMC was used as a solvent for the synthesis of several pharmaceutically relevant building blocks, i.e., *N*-Boc-3-pyrroline with yield similar to the previously reported synthetic procedures (86% vs 84.9%).[106]

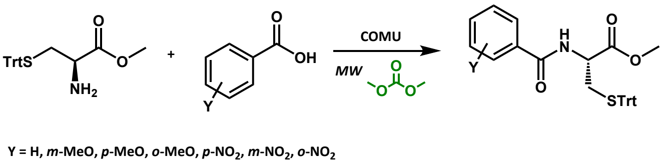
DMC displayed encouraging results also as solvent in substitution of 1,4-dioxane and toluene for the iron-catalysed one-pot hydrosilylation reaction of a wide range of *N*-alkylated and arylated cyclic amine derivatives including pharmaceuticals fenpiprane and prozapine (Scheme 10). Test reactions conducted with glutaric acid, aniline and DMC under visible light irradiation showed similar yield values to those performed using 1,4-dioxane and toluene (70%, 75% and 72% yield respectively).[107] Moreover, the use of $Fe(OTf)_2$ as an additive in some cases further increased the reaction yield of the desired cyclic amines up to 96%.[107]



Scheme 10. Synthesis of N-substituted cyclic amines using DMC as solvent.[107]

α-Substituted homoallylamines can be obtained using DMC and PC as solvents via a cationic 2-aza-Cope rearrangement of aldimines, generated *in-situ* by condensation of commercially available aldehydes and 1,1-diphenylhomoallylamines (81-98% products yield).[108]

DMC was also employed as a green substitute of dichloromethane in the microwave-assisted synthesis of peptidomimetics arylamides, compounds able to inhibit cysteine and serine-like proteases.[109] Overall, the yields obtained with the use of DMC (32-47%) were slightly lower when compared to those obtained when CH_2Cl_2 was used as solvent (44-70%), regardless of the coupling reagent employed (Scheme 11). Nevertheless, the isolation of the compounds when the reaction was performed in CH_2Cl_2 was hampered, due to the enhanced solubility of byproducts in this solvent.[109]



Scheme 11. Microwave-assisted synthesis of peptidomimetics arylamides in DMC. COMU: third generation uronium-type coupling reagent [(1-cyano-2-ethoxy-2-oxoethylidenaminooxy) dimethylamino-morpholino carbenium hexafluorophosphate].[109]

4.5 Wolff rearrangement/acylation reaction

DEC was employed as green solvent for the chemoselective cascade Wolff rearrangement/acylation reaction between 5-aminopyrazoles and diazo compounds (Scheme 12).[110] Among the different solvents tested - DCE, DMF, CH_3CN, dioxane, DMA, EtOH, tBuOH, BuOH, toluene, DMC and DMSO - carbonates media seemed to be particularly beneficial for in this reaction, with DEC and DMC giving yields up to 95% and 70%, respectively.[110]

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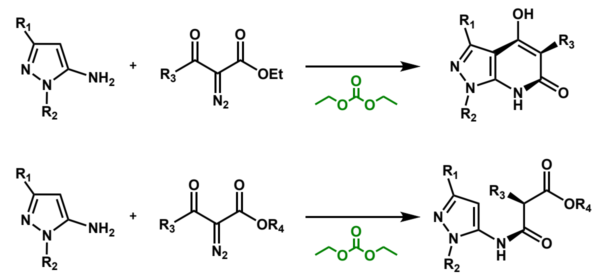


Scheme 12. Wolff rearrangement/acylation reaction between 5-aminopyrazoles and diazo compounds. [110]

4.6 Dehydration reaction: synthesis of 5-(hydroxymethyl)furfural

DACs such as DMC, DEC, PC and diallyl carbonate (DAllC) have been tested as co-solvents in several synthetic approaches to 5-(hydroxymethyl)furfural (HMF) – a well-known bio-based platform chemical - starting from D-fructose or D-glucose (Table 3). DMC was used in the reaction mixture as HMF extracting solvent; its use showed to reduce the formation of humins and the numerous byproducts (#1, Table 3).[112,113]

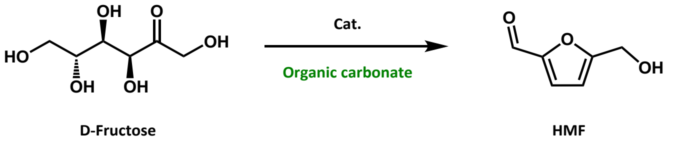
DMC can be also employed as the main reaction medium to achieve HMF either from D-fructose (#3, Table 3)[115117] or from more complex mixtures, i.e., cellobiose, sucrose, starch, corn-cob, sugarcane bagasse, rice-straw and corn-straw (#4-5, Table 3) even if in the latter cases with lower HMF yields.[114,116] The reason behind DMC utilization as media for sugar dehydration into furan-based molecules may lie in the enhanced stabilization capacity of compounds containing a carbonyl moiety i.e., methyl isobutyl ketone (MIBK), OCs and DMF towards furanics.[167,168] On this topic, a comprehensive study on the stability of different furan-based compounds both in acidic and basic media in the presence of various solvents was recently carried out by Ananikov and co-workers.[167]

4.7 Rh-catalysed reactions

The Rh-catalysed hydroformylation (oxo synthesis) of caryophyllene oxide and β-caryophyllene, was carried out employing DMC and DEC among other green solvents, replacing conventionally used hydrocarbons such as toluene and benzene (Scheme 13A).[120] Reactions showed high selectivity and complete substrate conversion despite a slightly lower reaction rate than the procedure conducted in toluene; whereas p-cymene performed with the same efficiency.[120]

Another suitable solvent for regioselective, Rh-catalysed hydroformylation reactions is PC, which showed to effectively mediate the isomerizing hydroformylation of *trans*-4-octene to *n*-nonanal in a two-phase catalytic reaction system (Scheme 13B). PC was able to increase the catalyst activity, leading to 95% conversion and up to 95% selectivity for the linear aldehyde.[118,119] On the other hand, tests performed employing PC/dodecane and PC/dodecane/p-xylene solvent mixtures showed that the higher the PC concentration, the higher the selectivity of *n*-nonanal. This significant influence of PC on the selectivity can be explained by the electron withdrawing effect of the carbonate group which may be able to interact with the β-hydride atoms of the σ-rhodium-complex, leading to a faster isomerization.[119]

Table 3. Organic carbonates as media for the synthesis of HMF from D-fructose.



#	Sugar	Solvent	Catalyst	T (°C)	t (h)	Conv. (%)	Selectivity HMF (%)	Yield HMF (%)	Ref.
1	D-Fructose	DMC/H_2O	CeP_3 (35% wt.)	150	6	73	93	68	112
		DEC/H_2O				49	88	45	
		PC/H_2O				46	85	40	
		DAllC/H_2O				43	80	36	
2	D-Glucose	DMC/ EMIMBr	$SnCl_4$ (10% mol.)	100	2	n.r.	n.r.	58	113
3	D-Fructose	DMC/TEAB	Amberlyst-15 (10% wt.)	90	5	99	n.r.	77	115
		DMC/TEAB	Purolite CT275DR (5% wt.)	110	2	n.r.	98	73	117
4	Corn-cob	DMC	$AlCl_3$ (30%wt.)/HCl (4N)	180	6	n.r.	n.r.	35	114
	Sugarcane bagasse					n.r.	n.r.	60	
	Rice-straw					n.r.	n.r.	37	
	Corn-straw					n.r.	n.r.	47	
5	D-Glucose	DMC	Sulfonated graphitic carbon nitride (S-GCN, 10% -50% wt.)	200	5	n.r.	99	23	116
	D-Fructose			200	5	n.r.	99	17	
	Cellobiose			200	5	n.r.	99	16	
	Sucrose			200	5	n.r.	99	30	
	Starch			200	5	n.d.	n.d.	n.d.	

n.r. : value not reported; n.d. compound not detected.

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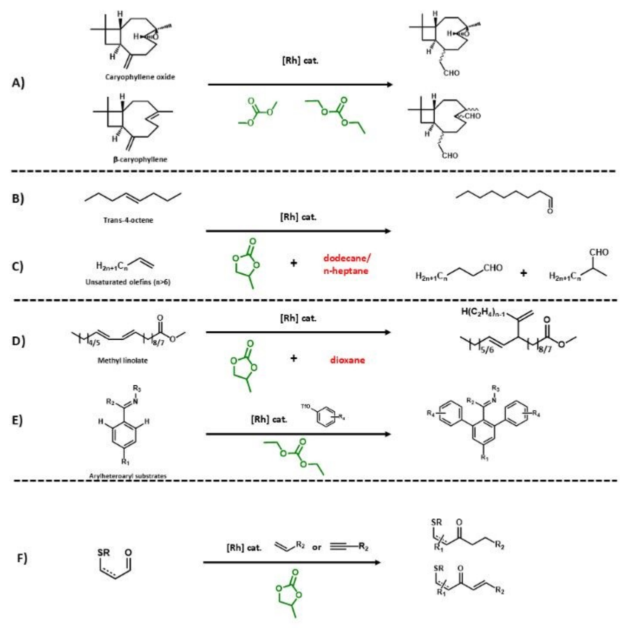
Similar results were achieved by Tijani and co-workers in the Rh-catalysed hydroformylation of higher olefins (C > 6), where a mixture of PC and *n*-heptane was reported as the most suitable solvent system (Scheme 13C).[121]



Scheme 13. A) Hydroformylation of caryophyllene oxide and β-caryophyllene[120]; B) Isomerizing hydroformylation of trans-4-octene to n-nonanal in a two-phase catalytic reaction system[119]; C) Rh-catalysed hydroformylation of higher olefins (C > 6), with a mixture of PC and n-heptane as solvent system[121]; D) Rh-catalysed co-oligomerization of fatty acid derivatives[118]; E) Rh- catalysed ortho-diarylation of various arylheteroaryl substrates with N-ligand employing DEC as green solvent[122]; F) Intermolecular alkyne hydroacylations using PC as solvent.[123]

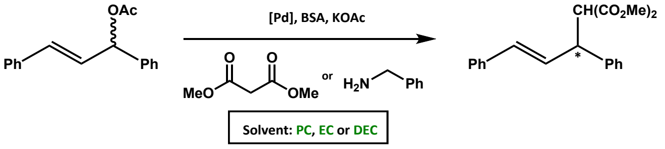
A solvent mixture of PC/ conjugated sunflower fatty acid methyl ester (SFAME)/1,4-dioxane was successfully employed in the Rh-catalysed co-oligomerization of fatty acid derivatives with ethylene, leading to internal branched fatty substances (Scheme 13D).[118] The total yield of the process can be increased to 98% in this solvent system under mild conditions (70 °C, 3.0 MPa) and the turnover frequency can be enhanced by factor 100 (2 vs. 220 h^{-1}).[118]

In addition, the selective ortho-diarylation of various arylheteroaryl substrates can be achieved by using N-ligand directed Rh-catalysed coupling of highly functionalized aryl phenolate derivatives employing DEC as green solvent in substitution of NMP and 1,4 dioxane (Scheme 13E).[122] Overall, using DEC as media allowed to yield the desired products even with bulkier, more hindered reagents as well as with electron-donating substituents in *para*-, *meta*- and *ortho*-position. [122]

Finally, PC was employed by Lenden et al. as green solvent for intermolecular alkyne hydroacylations, behaving as a valid alternative compared to DCE and acetone (Scheme 13F).[123] Results showed that these reactions could be carried out in PC using $[Rh(nbd)_2]BF_4$ as catalyst in combination with 1,2-bis(diphenylphosphino)ethane (dppe) as the ligand obtaining yields between 73 and 95%.[123]

4.8 Pd-catalysed reactions

Linear and cyclic OCs showed to be viable alternatives to chlorinated solvents also in Pd-catalysed transformations. As an example, PC, BC, and DEC were tested in substitution of CH_2Cl_2 in the Pd-catalysed asymmetric allylic substitution reactions of rac-1,3-diphenyl-3-acetoxy-prop-1-ene with dimethyl malonate or benzylamine as nucleophiles (enantioselectivities ranging from 83 to 98% - Scheme 14). The use of these green solvents in several cases led to enhanced yields and enantioselectivities compared to CH_2Cl_2.[124]



Scheme 14. Pd-catalysed asymmetric allylic alkylation of rac-1,3-diphenyl-3-acetoxy-prop-1-ene with dimethyl malonate or benzylamine using DACs as green solvents.[124]

Behr et al. investigated the substitution of CH_3CN as solvent with different linear DACs (DMC and DEC), cyclic DACs (EC, PC and BC), custom-made glycerol carbonate esters (glycerol carbonate propionate – GCP, glycerol carbonate butyrate – GCB) as well as DACs mixtures in the Pd-catalysed telomerisation of butadiene with carbon dioxide, leading to the formation of δ-lactone 2-ethylidene-6-heptene-5-olide (Scheme 15).[78]

Among the DACs tested, reactions conducted in PC and EC showed a higher selectivity (from 65 to ~90%, respectively) towards the lactone formation compared to linear carbonates and CH_3CN (*ca* 40% selectivity in the latter case). Reactions carried out in GCP and GCB showed lower yields of δ-lactone compared to EC, PC and BC, leading to the hypothesis that the selectivity of the lactone may depend on the size of the additional substituent in the carbonate solvent.[78]

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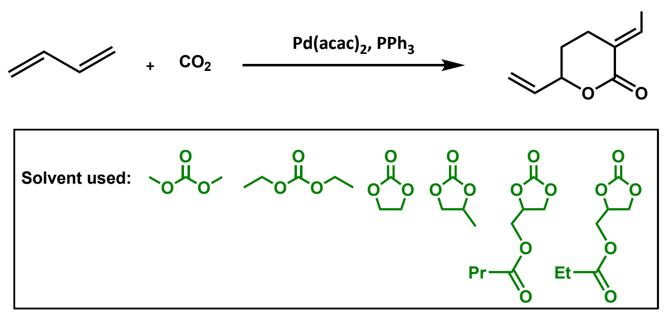
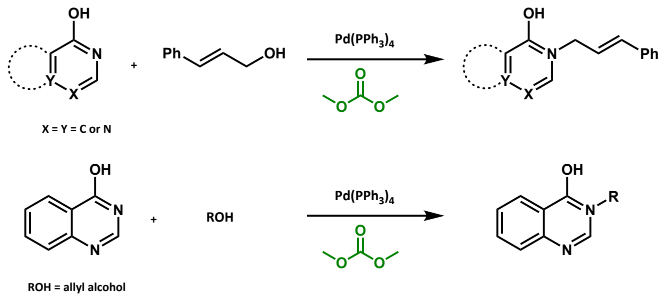


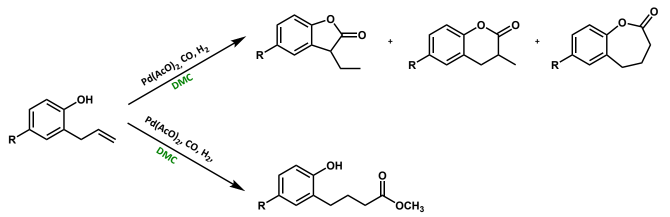
Scheme 15. Pd-catalysed telomerization of butadiene with carbon dioxide with DACs as solvents.[78]

DMC was proven to be an optimal green solvent for the chemo- and regioselective Pd-catalysed allylation of biologically relevant heteroarenes (Scheme 16).[125] Reactions displayed enhanced yield values of the allylated compound compared to DMF, 1,4-dioxane and CH_3CN (92%, 82%, 84% and 80% isolated yield, respectively).[125]



Scheme 16. Pd-catalysed allylation of biologically relevant heteroarenes with allyl alcohols.[125]

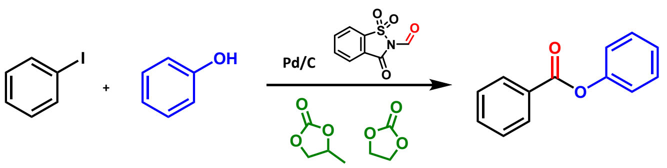
In addition, DMC was found to be a suitable replacement for toluene and CH_2Cl_2 in the selective cyclocarbonylation of allyl phenol derivatives for the synthesis of lactones (Scheme 17).[126] However it must be mentioned that in some cases DMC behaved as a ring-opening reagent producing methoxycarbonyl compounds when reactions were conducted for longer periods (48 h) and at higher temperatures (120 °C).[126]



Scheme 17. Cyclocarbonylation of allyl phenol derivatives for the synthesis of lactones with DMC as solvent.[126]

Partial Pd/C hydrogenation of a fatty acid methyl esters (FAME) mixture was performed in DMC as media by Quaranta and co-workers. However, in this case study lower conversion (37%) and selectivity values were obtained compared to when *n*-heptane was employed, under mild conditions (conversion and selectivity: 97.8% and 81.1%, respectively).[127]

Gautam et al. demonstrated that PC and EC can be used as green solvents for the Pd/C-catalysed phenoxycarbonylation of aryl iodides in the presence of N-formylsaccharin as CO surrogate, yielding a library of different phenyl esters (Scheme 18).[128] PC displayed higher substrate conversion compared to EC (76% and 67%, respectively), while complete selectivity towards the desired product was achieved in both cases.[128]

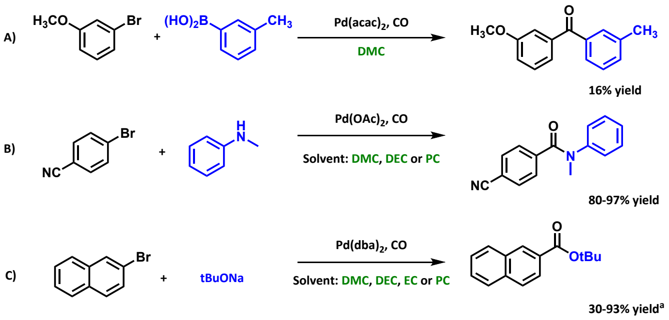


Scheme 18. Pd/C-catalysed phenoxycarbonylation of aryl iodides using DACs as solvents.[128]

Coupling reactions

Ismael et al. investigated the optimum solvent system for several Pd-catalysed carbonylative couplings namely, carbonylative crosscouplings (Scheme 19A), aminocarbonylations (Scheme 19B), and alkoxycarbonylations (Scheme 19C). Apart from the carbonylative crosscoupling between m-tolylboronic acid and 3-bromoanisole, in which the use of DMC led to a final yield of only 16% (Scheme 19A), all the other reactions could be successfully carried out using DACs as solvents such as DMC, DEC, EC and PC.[129] Specifically, the Pd-catalysed aminocarbonylation reaction of aryl bromides led to excellent yields employing DMC and DEC as solvents (97% and 94% yield, respectively); good results were also achieved in the presence of PC (80% yield; Scheme 19B).[129]

Pd-catalysed alkoxycarbonylation reactions instead gave the best results when performed in 2-Me-THF (91% yield) while DEC, EC and PC led only to moderate yields (45%, 30%, 60%, respectively; Scheme 19C). On the other hand, the reaction conducted in the presence of DMC, gave the methoxycarbonylated analogue in 93% isolated yield,[129] highlighting the capabilities of OCs as both reactants and reagents.[51]



Scheme 19. Pd-catalysed A) carbonylative couplings of m-tolylboronic acid and 3-bromoanisole; B) aminocarbonylation reaction of aryl bromides; C) alkoxycarbonylation reactions using DACs as media. ^{a}Reactions conducted in DMC led to the formation of the methoxycarbonylated analogue isolated in 93% yield. [129]

Suzuki-Miyamura and Sonogashira coupling

Among other green solvents, DEC and DMC showed to be viable alternatives in the Pd-catalysed Suzuki–Miyaura coupling of selected amides in substitution of THF (Scheme 20A).[130] The cyclic carbonate PC was also tested, without displaying encouraging results (37% yield). From a kinetic point of view, DACs showed a lower reactivity compared to other solvent tested such as i-PrOAc, cyclopentyl methyl ether (CPME) and methyl tert-butyl ether (MTBE).[130] Unfortunately, DEC displayed inconsistent yield values when both the starting amide and boronic acid were substituted with more hindered or electronically deactivated functional groups (yield values ranging from <5 to 89%).[130]

Several researchers employed PC as solvent in the Suzuki-Miyamura and Sonogashira coupling reactions. Czompa et al. reported that different heterocyclic compounds, i.e., 2-iodopyridine, 4-iodopyridine and 6-iodopyridazin-3(2H)-one and various boronic acids can be used as starting materials (Scheme 20B) both under microwave condition and conventional oil bath heating.[131] All reactions proceeded with good to excellent yields (from 43% to 92% under conventional heating and from 50% to 93% under microwave irradiation) of the corresponding coupling products. However, in the case of pyridazinones, 2-hydroxypropyl- chain containing side-products were observed due to the ring opening of the cyclic OC.[131]

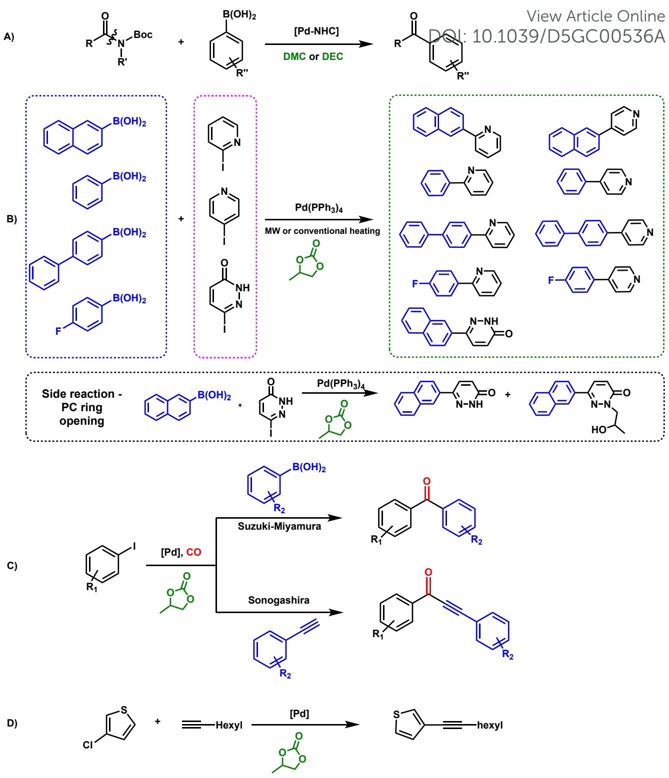
In another example, PC was used as media in the carbonylative Suzuki–Miyaura and Sonogashira cross-coupling reactions, catalysed by the aminophosphine pincer complex {[C_6H_3-2,6-(NHP{piperidinyl}$_2$)$_2$]Pd(Cl)}(III) (Scheme 20C).[135] In fact, carbonylation reactions are known to proceed efficiently in cyclic OCs which can thus be effectively employed in substitution of other toxic solvents, i.e., anisole, toluene, dioxane, DMA, MTBE, DMF.[135] Reactions proceeded with yields in the 70-80% range for both Sonogashira and Suzuki-Miyamura carbonylative cross-coupling. [135]

Finally, Torborg et al. employed PC as solvent for the Pd-catalysed Sonogashira cross-coupling reaction of aryl chlorides in the presence of N-substituted heteroaryl phosphines without copper co-catalysts (Scheme 20D).[134] The reaction of 3-chlorothiophene and 1-octyne was tested using PC as solvent at 90 °C leading to 76% yield of the cross-coupling product. It should be mentioned that PC can also partially displace the ligand, thus the reaction required higher Pd/ligand ratio. In contrast, the Sonogashira coupling in toluene with sodium carbonate as base yielded the desired 3-octinylthiophene in good yield at lower ligand concentration.[134]

Heck coupling

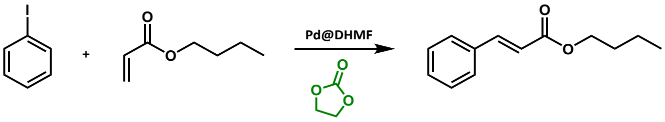
EC was found to be an excellent reaction media for Heck coupling, with complete substrate conversion and yields of up to 99% under microwave (MW) irradiation (Scheme 21). The Pd-based catalyst was supported on a humin-like resin obtained from 2,5-bis(hydroxymethyl)furan (DHMF) and maleic anhydride and successively encapsulated by in-situ polymerization.[133]

The same reaction was also tested in DMC, DEC and GC without obtaining comparable results (30%, 30% and 10% yield, respectively).



Scheme 20. A) Suzuki-Miyamura cross coupling of amides with DACs as media;[130] B) Suzuki-Miyamura coupling with different heterocyclic compounds using PC as solvent;[131] C) Carbonylative Suzuki–Miyaura and Sonogashira cross-coupling reactions in PC;[135] D) Sonogashira cross-coupling reaction of aryl chlorides in PC.[134]

The highest performance for EC was ascribed to its degradation and release of CO_2 upon heating, whose dissolution in the reaction media, facilitates Pd solubilization, as previously reported in literature.[169,170] This results in an increase of the reaction rate, because the Heck reaction occurs homogeneously in the organic phase. However, due to the thermal degradation of EC, its recovery and reuse cannot be performed.[133]



Scheme 21. Pd-catalysed Heck coupling reaction in EC as solvent. [133]

Other studies also reported the ability of PC to act as colloidal palladium stabilizer. Such colloidal solutions are then able to catalyse Heck reactions in the absence of phosphine ligands. Since catalysis is likely to occur on the surface of the clusters, these processes are probably more related to heterogeneous than to homogeneous catalysis.[171]

4.9 Ni-catalysed reactions

DMC was successfully employed as green media in substitution of toluene for the hydrodeacetoxylation of aryl acetates mediated by pinacolborane (HBpin) and a nickel-N-heterocyclic carbene (NHC) catalytic system, yielding the corresponding deoxygenated arenes (yields between 46 and 90%).[137]

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4.10 Pt-catalysed reactions

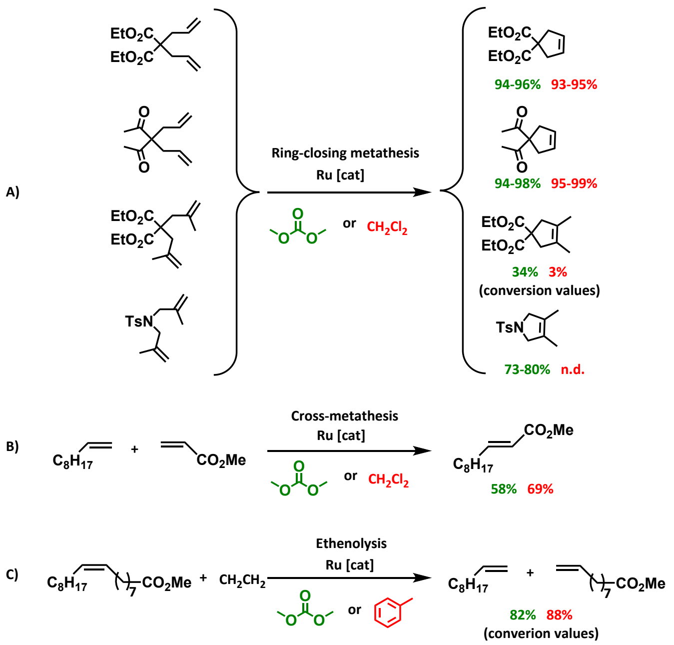
PC was applied as co-solvent in the platinum-catalysed hydrosilylation of unsaturated fatty acids.[138,139] In particular, the introduction of a ternary solvent system formed by cyclohexane/toluene/PC allowed the recycle and reuse of the catalyst even if hydrogenation and double bond isomerization of the starting reagent were reported to occur as side reactions.[138]

Moreover, a mixture of cyclohexane/PC and *n*-hexane/PC could be employed for catalyst recycling in these reactions.[138,139]

4.11 Ru-Catalysed Olefin metathesis

Olefin metathesis is almost exclusively carried out in dichloromethane and aromatic solvents (benzene, toluene, chlorobenzene). However, efficient metathesis transformations can be performed in DMC and PC, since they showed to be compatible with ruthenium-catalysed olefin metathesis reactions.[140–142]

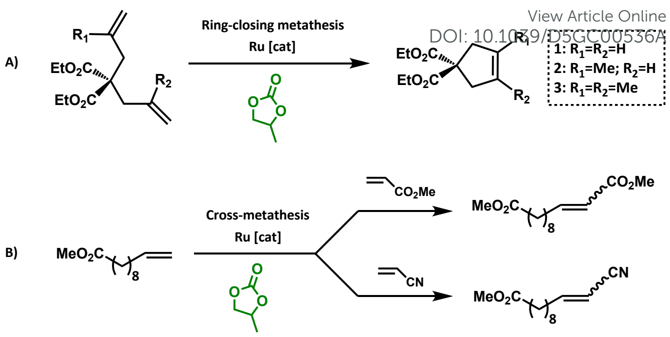
Miao et al. reported a series of olefin metathesis transformations, i.e., ring-closing metathesis (RCM), cross-metathesis and ethenolysis of methyl oleate, that can be performed in dimethyl carbonate and in CH_2Cl_2 (or aromatic solvents) with comparable results (Scheme 22). In some cases, RCM reactions proceeded faster in DMC than in CH_2Cl_2, despite displaying similar yield values.[140]



Scheme 22. Olefin A) ring-closing metathesis; B) cross-metathesis and C) ethenolysis in DMC.[140]

Huang et al. reported the use of PC as suitable solvent for the ruthenium RCM and cross-metathesis transformations of a variety of substrates including renewable fatty esters (Scheme 23).[141]

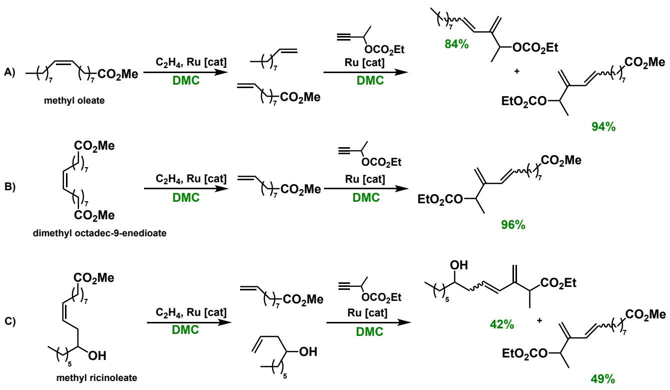
Ru-catalysed enyne cross-metathesis of several alkyne derivatives with terminal olefins can also be performed under mild conditions in DMC in substitution of dichloromethane and toluene.



Scheme 23. Olefin A) ring-closing metathesis and B) cross-metathesis in PC. [141]

A one-pot reaction based on an ethenolysis step followed by an enyne cross-metathesis allowed the efficient transformation of renewable unsaturated fatty esters into valuable conjugated 1,3-dienes.[142] This new reaction sequence provides a useful method in oleochemistry for the conversion of natural oils into functional compounds or intermediates of interest for further transformations.[142]

DMC was also employed as solvent, in substitution of toluene, in both ethenolysis and cross-metathesis reactions using different renewable fatty esters, i.e., methyl oleate (Scheme 24A), dimethyl octadec-9-enedioate (Scheme 24B) and methyl ricinoleate (Scheme 24C) yielding conjugated 1,3-dienes of interest for further transformations. The protocol allows the ene–yne cross-metathesis reaction to be carried out with long-chain terminal olefins and in one-pot with internal olefins after shortening by ethenolysis.[143]



Scheme 24. Two-step ethenolysis/ene–yne cross-metathesis starting from A) methyl oleate, B) dimethyl octadec-9-enedioate and C) methyl ricinoleate in DMC as solvent. Yields calculated via GC. [143]

In addition, cross-metathesis reactions of dec-1-ene and methyl undec-10-enoate with various terminal and internal propargylic acetates and carbonates were tested in toluene and DMC (yield values between 70-95% in the former case and from 54-74% in the latter one).[143]

4.12 Organic carbonates and ionic liquids as media in organic synthesis

The combination of ionic liquids and OCs as solvent systems consented to perform a wide variety of different organic

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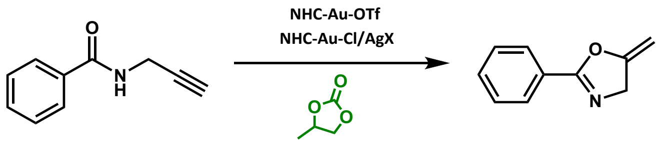
transformations. Particularly, cyclic DACs showed appreciable results for the synthesis of organic compounds in combination with ionic liquids. In fact, PC and supercritical CO_2 ($scCO_2$) were applied as solvents for the continuous synthesis of D,L-α-Tocopherol using sulfonic acid-functionalized ionic liquid as a catalyst (yields up to 90%). D,L-α-Tocopherol is the main composition of vitamin E and plays an important role in human health due to their antioxidative capacity and ability to act as free radical scavenger.[145]

Moreover, the cycloisomerization of N-(prop-2-yn-yl)benzamide to 2-phenyl-5-vinylidene-2-oxazoline in the presence of NHC-Au-X [NHC = (1,3-bis(2,6-di-isopropylphenyl)-imidazol-2-ylidene, X^- = BF_4^- , OTf^- ,OTs^- , TFA^-] as catalysts was carried out in PC, among others, as media (Scheme 25).[146] However, it must be mentioned that in this case green solvents showed, on average, slower conversion with respect to volatile organic solvents (VOS) ($Conversion_{PC}$: 49%, TOF_{PC}: 180 h^{-1} vs. Conversion $_{CH2Cl2}$: 89%, TOF $_{CH2Cl2}$:406 h^{-1}).[146]



Scheme 25. Cycloisomerization of N-(prop-2-yn-yl)benzamide to 2-phenyl-5-vinylidene-2-oxazoline in the presence of NHC-Au-X in PC. [146]

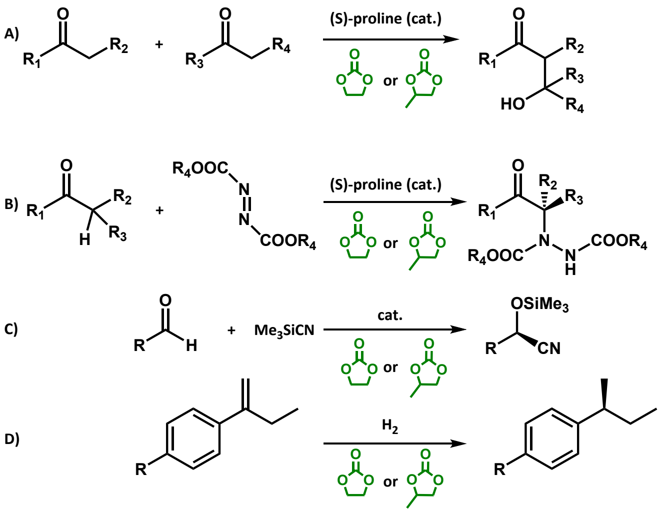
The vitamin B1 like-derived acidic ionic liquid $[HMTH]_2H_2[SiW_{12}O_{40}]$ coupled with DMC, PC and EC as solvents, was found to be an efficient heterogeneous catalyst for the direct dehydrative coupling of alcohols with alcohols or alkenes to synthesize various polysubstituted olefins. Excellent yields of the desired compounds were obtained (93% yield at 120 °C for 15 min, 3% catalyst loading) with DMC as a green solvent while the reaction proceeded with good yields in PC and EC (66% and 37%, respectively).[132]

4.13 Phase transfer catalysis

DMC was tested together with methyl-tert-amyl ether (MTAE), 5-methyl-2-hexanone (MIAK) and MIBK as alternative media to toluene and chlorobenzene for phase transfer catalysed (PTC) reactions in organic media. Experiments were conducted by putting in contact different quaternary ammonium salts (Q^+Y^-), i.e., $MeBu_3N^+Cl^-$, $MeBu_3N^+$ p-$NO_2C_6H_4O^-$, $Bu_4N^+Cl^-$, $Bu_4N^+Br^-$, Bu_4N^+p-$NO_2C_6H_4O^-$, $Hexyl_4N^+Cl^-$, $Hexyl_4N^+Br^-$, $Hexyl_4N^+$p-$NO_2C_6H_4O^-$, $Octyl_3MeN^+Cl^-$, $Octyl_4N^+Br^-$, $Bu_3P^+C_{16}H_{33}Br^-$ dissolved in the selected organic media and a water solution containing the corresponding sodium salt (Na^+Y^-). Data showed that in these media the partition of the catalyst in the organic phase is comparable or higher than that in chlorobenzene.[147] In particular, the solubility in DMC is similar with that in chlorobenzene under both homogeneous and heterogeneous conditions and hence DMC represents a valid greener alternative to the solvents traditionally used in PTC processes.[147]

4.14 Enantioselective reactions

EC and PC have been showed to be excellent media for several asymmetric reactions, i.e., aldol reactions,[151,172,173] hydrogenation of non-functionalized olefins,[148,149] cyanohydrin trimethylsilyl ethers synthesis,[150] and α-hydrazination of aldehydes and ketones[152] in substitution of the most employed toxic solvents such as DMF, DMSO, CH_2Cl_2 and CH_3CN (Scheme 26). In all cases, chemical yields up to 99%, diastereoselectivities up to 100% and enantioselectivities up to 99% was obtained.[151]



Scheme 26. Asymmetric reactions using EC and PC as green solvents: A) asymmetric aldol reaction; B) α-hydrazination of aldehydes and ketones; C) cyanohydrin trimethylsilyl ethers synthesis; D) asymmetric hydrogenation of non-functionalized olefins.

4.15 Photocatalytic reactions

Photocatalytic reactions were reported in the literature using DMC as media under both UV and visible light irradiation (Table 4, Scheme 27).

A transition-metal-free photocatalytic decarboxylative 3-alkylation reaction of 2-aryl-2H-indazoles was developed under visible-light irradiation (#1, Table 4; Scheme 27). By employing 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) as photocatalyst, and alkyl N-hydroxyphthalimide esters as alkylating reagents, various primary, secondary, and tertiary alkylated 2-aryl-2H-indazoles were synthesized in moderate to good yields (41-91%). 2-Aryl-2H-indazoles containing strong electron-withdrawing substituents (4-NO_2 and 4-CN) showed no reactivity in these conditions. Moreover, the protocol was successfully applied to the late-stage modification of drug molecules such as Pazopanib, ER-16b, Niraparib, and WAY-214950.[153]

Furthermore, DMC showed to be a suitable solvent for i) the direct CH bond arylation of anilides later applied for the gram-scale synthesis of the fungicide Boscalid (81% isolated yield; #2, Table 4)[154]; ii) the aerobic oxidative hydroxylation of boronic acids (#3, Table 4)[158]; iii) the oxidation of diverse alcohols (#4, Table 4)[157] and iv) the synthesis of 1,3-diene derived quinolinone compounds (#5, Table 4).[159]

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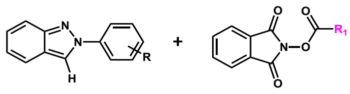
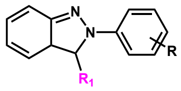
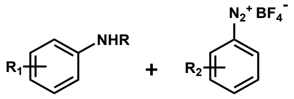
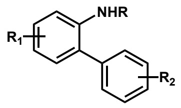
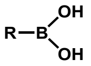
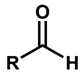
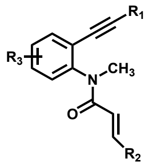
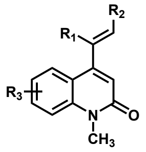
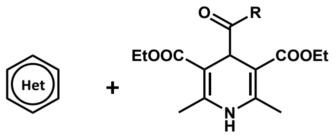
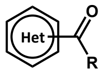
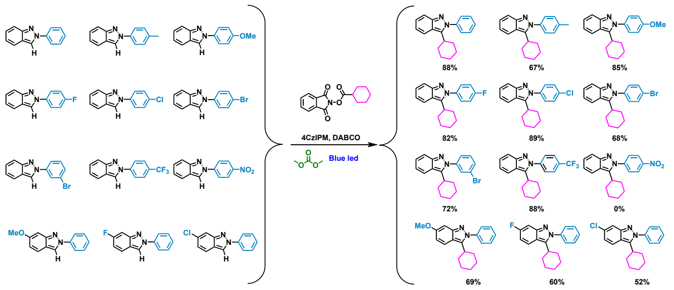
Table 4. Photocatalytic reactions performed with organic carbonates as media.

#	Reaction type	Organic carbonate	Reagent(s)	Product(s)	Catalysts	Yield (%)	Ref.
1	Decarboxylative 3-alkylation	DMC	 2-aryl-2H-indazoles, alkyl N-hydroxyphthalimide esters		4CzIPN, blue led	41-91	153
2	CH bond arylation	DMC	 anilides, aryldiazonium salts		$Ru(bpy)_3Cl_2$, $Pd(OAc)_2$, visible light	67-94	154
3	Oxidative hydroxylation	DMC	 Boronic acids	R—OH	7H-benzo[c]thioxanthen-7-one, visible light	81-97	158
4	Alcohol oxidation	DMC	R—OH		TiO_2(C/T), visible light	64-95^a 92-99^b	157
5	1,3-diene derived quinolinone compounds	DMC			4CzIPN, blue led	13-93	159
6	Aroylated heterocycles	DMC	 heterocycles, acyl-DHPs		Catalyst free, visible light, blue led	40-95	156

^{a} Conversion values. ^{b} Selectivity values.

Additionally, Zeng and co-workers developed a visible-light-induced strategy for the construction of various aroylated heterocycles, including the modification of pharmaceuticals and natural products, i.e., thioflavones, benzimidazo[2,1-a]isoquinolin-6(5H)-ones, indolo[2,1-a]isoquinolin-6(5H)ones, quaternary 3,3-dialkyl 2-oxindoles, quinoxalin-2(1H)-ones, and benzo[e][1,2,3] oxathiazine 2,2-dioxides in DMC (#6, Table 4).[156]



Scheme 27. Examples of 3-alkylation of 2-aryl-2H-indazoles in DMC. [153]

4.16 Other Reaction/Applications of organic carbonates as media in Organic synthesis

Condensation/rehydration reaction

The perfume additive Florol® is widely used in the fragrance industry and could be synthesized via a condensation and rehydration reaction starting from isoprenol and isovaleraldehyde using DMC as a solvent. The reaction was performed in the presence of microporous H-Beta-300 with SiO_2/Al_2O_3 ratio of 300 (72% selectivity and 99% conversion) at 40 °C.[160]

Radziszewski reaction

PC was employed as alternative media for the preparation of 2,4,5-triaryl imidazoles in the Radziszewski reaction, in substitution of DMSO and DMF (Scheme 28). A wide range of 2,4,5-triaryl substituted imidazoles were synthesized. PC offered advantages not only in the yield of the reaction but also

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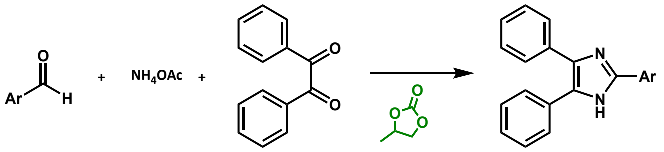
in the isolation of the product, which consists of a simple filtration followed by washes with warm water.[161]



Scheme 28. Synthesis of 2,4,5-triaryl imidazoles via Radziszewski reaction with PC as media. [161]

Cyclodextrin-based supramolecular assemblies

DEC and methanol were used as to fabricate 2-O-methylated β-cyclodextrin (2-Me-β-CD)-based supramolecular assemblies with diverse morphologies on a polyethylene terephthalate (PET) substrate.[162]

Complexation reactions

PC and its mixtures with other solvents, i.e., DMF, H_2O and MeOH were studied as media for the complexation reaction between UO_2^{2+} cation with diaza-15-crown-5 (DA15C5) using the conductometric method. The stability order of $(DA15C5.UO_2^{2+})$ complex in pure studied solvents was found to be: PC > H_2O > DMF » MeOH. [163]

Claisen rearrangement

Thermal aromatic Claisen rearrangement of allyl-aryl ethers to obtain ortho-allyl phenols (naphthols) was performed employing PC as solvent. Reactions performed in PC allowed to increase product yields (70-83%) and reduce significantly the reaction time (1-6h) comparing with the use of 1,2-dichlorobenzene (DCB; 52-75%; 10-40 h), traditionally employed in this type of Claisen rearrangement.[164]

Ring-opening reactions

Righi et al. showed that several ring-opening methodologies catalysed by $MgBr_2$, LiBr/Amb15, NaBr/Amberlyst-15 and $BF_3{\cdot}Et_2O/TMSN_3$ could be performed in DMC in substitution of the usually employed solvents, i.e., dichloromethane, Et_2O and CH_3CN. In the new developed procedures, the stereo- and regioselectivity is conserved and the work-up results simplified requiring just a filtration, therefore reducing considerably the amount of solvent employed in the processes.[165] Substrates employed with these methodologies comprised: epoxy alcohols, silylated aziridino alcohols, epoxy- and aziridino esters, and vinyl epoxides and vinyl aziridines.[165]

All the reactions were performed at room temperature, and the only noticeable difference is in the reaction times (10 h DMC vs. 2–4 h Et_2O; 1–2 h DMC vs. 5 h CH_3CN) while product isolated yields varied from 70 to 99%.[165]

5. Organic carbonates in polymerization and depolymerization reactions

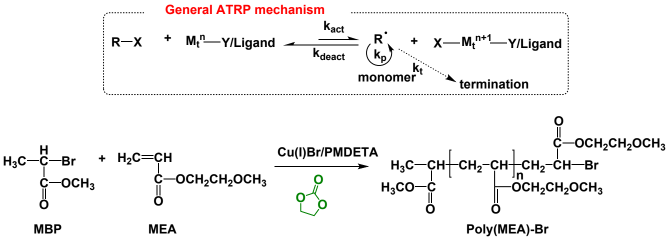
OCs such as PC, EC, DMC have been efficiently employed for different types of polymerizations,[174–178] including electroploymerization,[179–188] photopolymerization,[189,190] as well as depolymerization reactions. Regarding the latter topic studies have been reported on the depolymerization of cellulosic paper towels,[191] solvolysis of cellulose,[192] liquefaction of newspaper[193] and lignin depolymerization.[194]

5.1 Radical polymerizations

An example of radical polymerization conducted in OCs is the copolymerization to polyethylenes with low ketone content that was carried out using DMC or under aqueous conditions at pressures <350 atm.[177]

DACs/water biphasic systems composed by DEC, DMC, PC and EC showed to be suitable also for Single Electron Transfer Living Radical Polymerization (SET-LRP) in substitution of THF and 1,4-dioxane.[176] The SET process involves the transfer of a single electron from an electron donor (i.e., Cu(0) and Cu(I)X catalysts) to an electron acceptor which can be situated in two different molecules or in two sites of a single compound.[195] This mechanism can be exploited for the promotion of different chemical transformations in biology, electrochemistry and polymer chemistry.[195] DEC as well as other nonpolar solvents i.e., ethyl acetate, toluene, anisole, and cyclohexane showed to mediate the SET-LRP of n-butyl acrylate (BA) in ethanol/water mixtures at a 4.0:4.0:2.0 volume ratio in substitution of hexane.[175]

In a similar fashion, EC was investigated as solvent in the Atom Transfer Radical Polymerization (ATRP).[174] In ATRP, the radical species are generated through a reversible red-ox process catalysed by a transition metal complex (M_t^n–Y/Ligand, Scheme 29, top side). This process is regulated by activation (k_{act}) and deactivation (k_{deact}) constants. Similarly to radical polymerization mechanisms, polymer chains propagate by the addition of the intermediate radicals to monomers (constant of propagation, k_p). Moreover, in ATRP, termination reactions (termination constant, k_t) can rarely occur majorly through radical coupling and disproportionation.[196]



Scheme 29. General mechanism for ATRP (top) and ATRP of MEA in EC as media. [174,196]

In an example, the ATRP of 2-methoxy ethyl acrylate (MEA) was carried out in the presence of methyl 2-bromopropionate (MBP) as initiator and CuBr/N,N,N0,N0,N00-pentamethyldiethylenetriamine (PMDETA) as catalyst system (Scheme 29, bottom side).[174] The resulting polymers were compared to those obtained using toluene as media, showing similar results in terms of M_n and M_w/M_n. In addition, polymers both displayed a narrow molecular weight distribution.[174]

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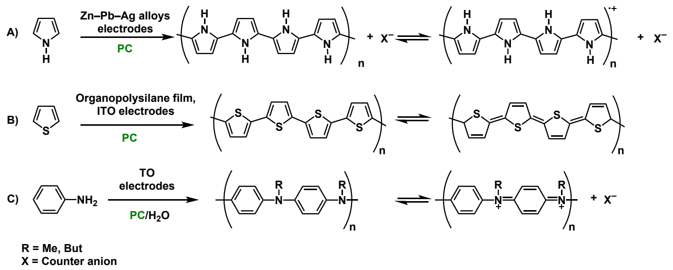
5.2 Electropolymerizations

Electropolymerization techniques allow to produce polymeric or inorganic films with precise spatial resolution by using three standard configuration electrodes (working electrode, reference electrode, and counter electrode) in an electrochemical cell, dipped in an electrolytic solution (Scheme 30). After the potential is applied, a polymeric thin film starts growing onto the working electrode surface.[197,198]

Polymers obtained can be used for batteries, conductive textiles and fabrics, antistatic coatings, supercapacitors and special sensors.[179] It should be mentioned that the solvent affects the electrochemical activity, conductivity, and morphology of the resulting polymer.[199] Therefore, the solvent choice is particularly important since it provides an ionic conducting medium. It must possess a high relative permittivity and it must be stable at the oxidation potential of the monomer. PC was reported to be an ideal solvent since it fulfils all these characteristics.[179]



Scheme 30. Electropolymerizations using DACs as media. A) Pyrrole electropolymerization;[200] B) thiophene electropolymerization;[201] C) N-methylaniline (NMA) and N-butylaniline (NBA) electropolymerization; mechanism modified from. [184] ITO: indium tin oxide, TO: tin oxide.

Pyrrole electropolymerization

Electropolymerization in PC is mainly utilized for monomers like pyrrole, thiophene, and aniline derivatives, but some applications can also be found for styrene[185] and acetylenes.[186,187] Several works reported pyrrole electropolymerization on zinc[180] and zinc-lead-silver alloy[181] electrodes in PC. The use of this media in the presence of p-toluene sulfonate counterions showed improved results compared to other solvents, i.e., CH_3CN and nitrobenzene obtaining high quality, homogeneous and thick coatings (Scheme 30 A).[181]

Polythiophene and 2,2′-bithienyl electropolymerization

Many derivatives of thiophene[182] and bithiophenes[183] were used as substrate for electropolymerization in PC. As an example, Tachibana and co-workers achieved a conductive fine line patterns after electropolymerization of dissolved UV-exposed polysilanes (Scheme 30 B).[182] Notably, PC was suitable for 2,2-bithiophene electropolymerization, revealing that despite the reaction was thermodynamically and kinetically favoured in CH_3CN, better morphologies and enhanced mechanical stabilities could be obtained in PC.[183]

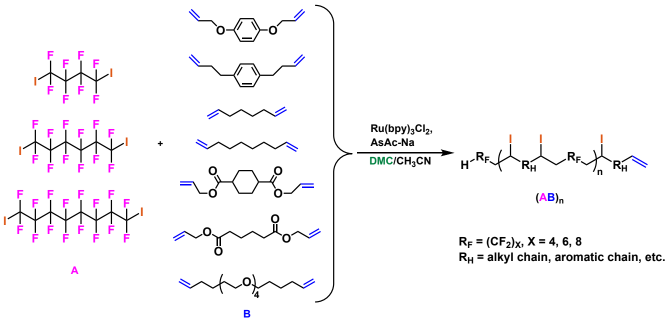
Moreover, electropolymerization of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) and tetrafluoroborate was carried out in PC as media to create coatings for metal electrodes which possessed similar proprieties to those obtained in CH_3CN. Coatings prepared with PC displayed excellent electrochemical stability and survived autoclave sterilization, prolonged soaking, and electrical stimulation without major changes in electrochemical properties.[188]

Aniline and methyl aniline electropolymerization

Mixtures of PC and water (80% water; 10-20% PC) showed to enhance N-methylaniline (NMA) and N-butylaniline (NBA) electropolymerization yielding narrower molar weight distributions and higher electrical conductivities compared to when DMF and DMSO mixtures were employed (Scheme 30 C).[184]

5.3 Photopolymerizations

DMC/CH_3CN solvent system favoured the photoinduced polyaddition reaction between α,ω-diiodoperfluoroalkanes and α,ω-unconjugated dienes instead of chain transfer ones, generating high yielding (76.5%) and high molecular weight ($M_{n,GPC}$ = 9400 g mol^{-1}) of perfluorocarbon-containing alternating copolymers. The polymerization was performed under irradiation with blue light emitting diodes (LEDs) at room temperature (25 °C, Scheme 31).[189]

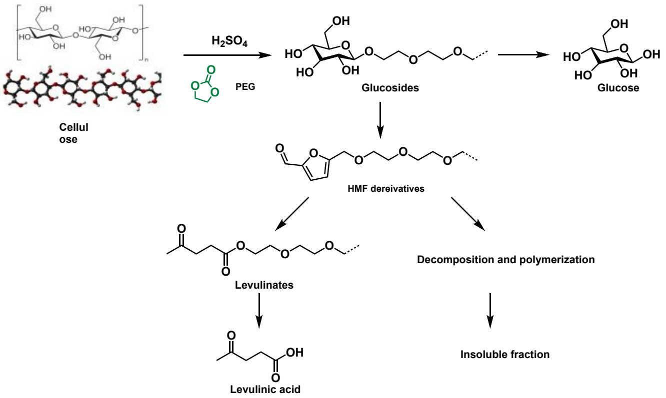


Scheme 31. Photoinduced step transfer-addition & radical-termination (START) polymerization between α,ω-diiodoperfluoroalkanes and α,ω-unconjugated dienes in a mixture of DMC and CH_3CN as media.[189]

Kim et al. reported DMC as the most efficient solvent among more than 40 others for the free radical photopolymerization of alkenes, including vinylidene fluoride (VDF), vinyl acetate, methyl methacrylate, styrene, and butadiene.[190]

5.4 Depolymerization

Degradation and decomposition of cellulose were studied in an acid-catalysed solvolysis treatment of biomass using polyethylene glycol (PEG) and EC. EC showed to promote a faster degradation of cellulose compared to PEG, leading to the formation of glucosides, which then decompose, resulting in a levulinic acid structure (Scheme 32).[192] DMC was instead employed as trapping agent for EG in the depolymerization of polyester fibres from textile products.[202]

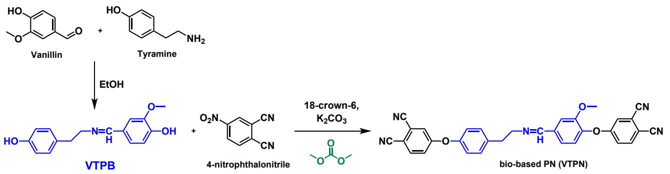


Scheme 32. Acid-catalysed solvolysis for the decomposition of cellulose in an EC-PEG system.[192]

Furthermore, PC, EC, DMC and their mixtures with water were investigated as green co-solvents for the MW-assisted depolymerization of cellulosic paper towel waste catalysed by dilute sulfuric acid in substitution of DMSO and THF. PC/H_2O and EC/H_2O enhanced the depolymerization of paper towel waste and improved the total sugar yield (up to *ca* 25 C mol %) compared to H_2O only (up to *ca* 11 C mol %) under mild reaction conditions (130 °C, 20 min). The higher performance of PC/H_2O and EC /H_2O can be attributed to higher availability of reactive protons in the catalytic system that facilitates efficient acid hydrolysis of recalcitrant cellulosic fibres.[191] However, the high boiling point (242–248 °C) of these solvents can be challenging for product separation and solvent recovery by distillation.[191]

5.5 Resin preparation

DMC proved to be useful as solvent in the synthesis of a bio-based phthalonitrile (PN) resin, prepared via a nucleophilic substitution reaction between 4-nitrophthalonitrile and Schiff base bisphenol (VTBP, obtained by reacting vanillin and tyramine in ethanol) (Scheme 33). To further increase the sustainability of the procedure, DMC was recovered and reused.[203]



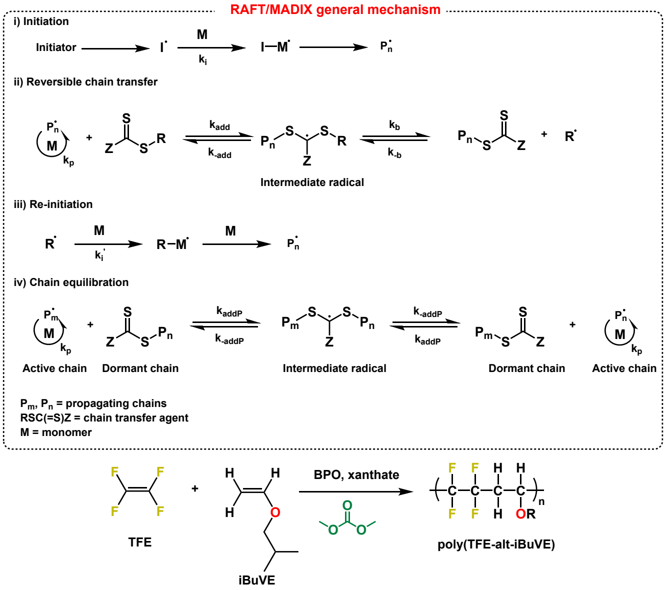
Scheme 33. Synthesis of a bio-based phthalonitrile (PN) resin (VTPN) via a nucleophilic substitution reaction between 4-nitrophthalonitrile and Schiff base bisphenol (VTBP). VTPB was obtained by reacting vanillin and tyramine in ethanol.[203]

5.6 RAFT/MADIX co-polymerization

DMC was used as media for the co-polymerizations reactions between tetrafluoroethylene (TFE) and isobutyl vinyl ether (iBuVE), via both conventional radical and Reversible Addition–Fragmentation Chain Transfer Polymerization/Macromolecular Design via the Interchange of Xanthates (RAFT/MADIX) methods.[204] RAFT/MADIX method allows to control chain growth in radical polymerization through a dynamic equilibrium between growing chains and dormant ones based on reversible transfer or termination reactions (Scheme 34). This technology can be used to design complex functional architectures in bulk, in organic solvents and water.[205]

In particular, O-ethyl-S-(1-methyloxycarbonyl)ethyl xanthate and benzoyl peroxide (BPO) were used as RAFT chain transfer agent and initiator, respectively, yielding alternating copolymers (poly(TFE-alt-iBuVE)) (Scheme 34). Molar masses varied between 11000 and 4400 g mol^{-1} with broad dispersities (Đ = 2) with the conventional method and from 1200 to 2000 g mol^{-1} and narrower Đ (1.08 - 1.11) via RAFT/MADIX.[204]

Furthermore, Guerre et al.[206] demonstrated that radical DMC fragments were generated during vinylidene fluoride (VDF) polymerization through a proton transfer process. This may initiate a further polymerization or terminate other macroradicals by recombination.[204] Proton transfer from DMC or the vinyl ether monomer onto the macroradical was observed in uncontrolled copolymerization, whereas much less proton transfer from DMC was noted in RAFT copolymerization.[204]



Scheme 34. RAFT/MADIX general mechanism (framed reactions); co-polymerization between tetrafluoroethylene (TFE) and isobutyl vinyl ether (iBuVE), via RAFT/MADIX in DMC as media.[205,204].

5.7 Polymer crystallization

In a reported study poly(2-isopropyl-2-oxazoline) (PIPOx) crystallization was performed in either DMSO or PC, generating polymers with a higher crystalline content than PIPOx crystallized in CH_3CN.[207]

In addition, porous structures were prepared by extrusion-based 3D printing of biodegradable PCL-b-PTMC-b-PCL triblock copolymers based on trimethylene carbonate (TMC) and ε-caprolactone (CL) using EC as a crystallizable and water-extractable solvent.[208]

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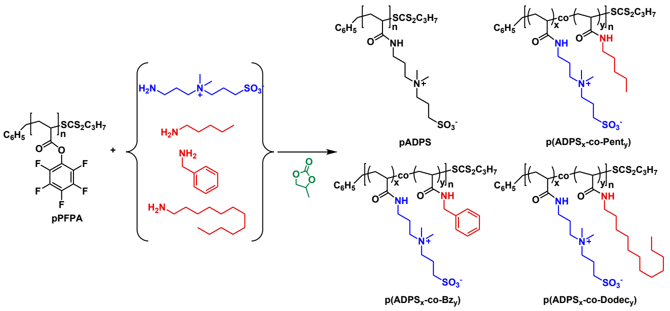
5.8 Post-polymerization Modifications

Woodfield and co-workers presented a post polymerization modification to prepare sulfobetaine co-polymers by employing an activated ester precursor, poly-(pentafluorophenyl acrylate), a zwitterionic amine, 3-((3-aminopropyl)dimethylammonio) propane-1-sulfonate, ADPS (and ADPS mixtures with other amines) with PC as solvent.[209] The scope of activated esters was also investigated, thus providing synthetic access to a library of well-defined hydrophobically modified zwitterionic co-polymers.[209]

5.9 Lignin-derived polymers

DMC was employed as a solvent in substitution of dichloromethane for the curing of lignin and plant oils via olefin metathesis to produce thermosetting polymer films. Resulting materials displayed similar Young's moduli and tensile strength, but those produced with DMC showed a lower degree of cross-linking compared to the films produced in CH_2Cl_2.[194] Diallyl carbonate (DAllC) was also used as media to suspend organosolv lignin (OL) and prepare allylated lignin.[194]



Scheme 35. Sulfobetaine co-polymers via poly(pentafluorophenyl acrylate), pPFPA as activated ester in combination with ADPS and other amines in PC as solvent.[209]

5.10 Polyurethane (PU) adhesives preparation

Polyols, which are important compounds of polyurethane adhesives (PU), were prepared by liquefying beech wood sawdust[210] and hardwood residue (HR)[211] with EC and sulfuric acid. The obtained bio-polyol was used for two kinds of PU adhesive by blending two types of isocyanate, poly4,4'-diphenyl methane diisocyanate (PMDI) and toluene diisocyanate (TDI), in different NCO/OH ratios for the preparation of polyurethane adhesives.[210] EC can restrain the free radical produced by the lignin fragments and then stop the recondensation in the liquefaction process.[211] On this topic, Yamada and Liang [212,213] reported that the rate of liquefaction of cellulose and hardwood in EC and PC is almost 30 times faster than other solvents such as polyhydric alcohols, probably due to the high permittivity of cyclic carbonates.[210]

5.11 Microencapsulation

DMC and PC were used as solvents to fabricate poly(D,L-lactide-co-glycolide) (PLGA) microspheres[214] and nanoparticles, respectively.[215] In the former case, DMC was employed as a green dispersed solvent, creating an oil-in-water emulsion made by PLGA/Nile red/progesterone/DMC in an aqueous phase. The subsequent addition of a NaOH solution into the emulsion led to the decomposition of DMC that partitioned to the water phase thus allowing the continuous diffusion of DMC existing in emulsion droplets into the aqueous phase and its complete removal. This process allowed the uniform distribution of Nile red across the microsphere matrix. In addition, a drug crystallization phenomenon commonly observed in conventional emulsion-templated processes, was inhibited by increasing the hydrolysis rate of DMC. The green solvent hydrolysis-based microencapsulation technique could be a promising alternative to conventional microencapsulation methods using toxic halogenated organic solvents.[214]

In addition, small transparent PLGA nanoparticles (below 70 nm) were obtained by an emulsification-diffusion method employing – among others - PC as media. On the other hand, larger PLGA nanoparticles (above 290 nm) were obtained using acetone and CH_2Cl_2.[215] Small particle sizes for PC were attributed to both the adequacy of the stabilizer's protection against coalescence, and the low interfacial tension between aqueous and organic phases, resulting from their partially water-soluble nature.[215]

6. Organic carbonates in CO_2 capture

The combination of DMC as a solvent and either polydimethylsiloxane (PDMS)/TiO_2 or (PDMTS)-SiO_2 nanocomposites can be used as a CO_2 capture method due to DMC high CO_2 solubility and low desorption.[216–218] In this process, CO_2 is initially absorbed in DMC, and then CO_2 is desorbed by a pervaporation (PV) membrane from the rich liquid solvent allowing *ca* 72% of energy savings compared to conventional CO_2 capture methods.[219] In addition, diethylenetriamine (DETA) dissolved in different solvents - ethanol, diethylene glycol dimethyl ether, NMP or DMC - can be effectively used as a CO_2 absorber. Single crystals of DETA-carbamate indicated that one mole DETA can absorb one mole of CO_2 to form precipitates in organic solvents.[220]

DEC was also shown to perform as a good CO_2 absorbent with even better results in terms of liquid-gas ratio, absorption temperature, desorption temperature and N_2 flow on CO_2 absorptivity compared to DMC.[221]

For these reasons, DMC and DEC were tested as additives to dimethyl ethers of polyethylene glycol (DEPG) for the removal of acid gas like CO_2 and H_2S in the Selexol™ process due to their strong CO_2 adsorbing characteristics.[222–224] Results showed that the addition of DMC and DEC led to reduced net utility costs compared to the normal Selexol™ process. However, a major drawback of DMC and DEC is the vast solvent loss during the solvent regeneration stage. This increases the solvent make-up cost by too much for them to be economically competitive. [224]

On the other hand, PC showed promising performances as physical absorbent for biogas upgrading, with a 30% specific cost reduction compared to when water is employed.[225]

7. Organic carbonates as solvents for membranes, films and fibres preparation

The intrinsic proprieties of membrane-based processes make them a simple, flexible, selective and an environmentally friendly technology which requires low energy consumption as well as simple scale-up and operational conditions.[226–228] Membrane processes are effectively employed in a wide variety of industrial applications including the separation of complex mixtures, hydrogen isolation[229] and CO_2 removal,[230] wastewater treatment[231] and water desalination,[232,233] allowing up to 50% of energy savings on the production cost compared to other traditional separation technologies.[230] Nevertheless, most of the commonly employed solvents in this field - NMP, DMF and DMA - display cancerogenic and teratogenic effects,[234] present high volatility and thus represent a threat to the ecosystem and human beings.[235,236]

Replacing traditional toxic solvents with greener alternatives is not an easy task, since they have a particular set of properties that play a crucial role in determining the final membrane morphology and performance.[237] Solvent properties such as viscosity, dielectric constant, polarity and boiling point greatly affect membrane characteristics imparted in their formation.[236]

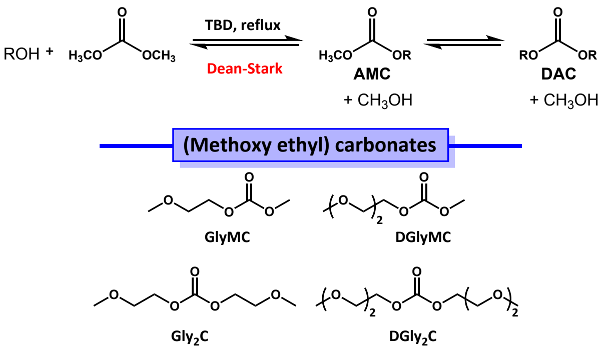
In this scenario, traditional solvents need to be replaced with greener ones possibly synthesized in a sustainable way.

One of the possible solutions for these issues is the employment of OCs.[35,238] In fact, it has been reported that replacing NMP with EC in the preparation of PVDF membranes significantly reduced the overall environmental impact by up to 35% according to life cycle assessment analyses.[237]

Rasool and co-workers employed commercially available DMC, DEC, PC, 1,2-butylene carbonate, GC and the custom made 1,2 hexylene carbonate and styrene carbonate (SC) as green solvents for membrane preparation using different polymers such as polyethersulphone (PES), polyacrylonitrile (PAN) polyvinilydene fluoride (PVDF) etc.[238] Due to solubility issues of most polymers in OCs, several mixtures were investigated in order to obtain suitable polymer-solvent compatibility for membrane casting, (homogeneous polymeric solution). Investigated examples include OC/OC (i.e., SC/PC), OC/NMP and OC/methyl lactate.

7.1 Polyvinylidene fluoride membranes

Linear water-soluble OCs can be employed as green media for polyvinylidene fluoride (PVDF) membranes preparation both via non-solvent induced phase separation (NIPS) and a combination of vapor induced phase separation (VIPS)-NIPS techniques (Scheme 36). Phase inversion techniques involve the transformation of a polymeric solution into a solid polymeric matrix which, in the case of NIPS, is achieved by the immersion of a cast polymeric solution in a non-solvent bath, while in VIPS by the non-solvent vapor present in a climatic chamber.[226,239] Phase inversion methods are among the most employed processes to prepare commercially available membranes. These methods are very versatile and allow to produce membranes with different morphologies.[239] Membranes obtained with custom-made DACs displayed greater structural resistance and a smaller pore size compared to ones achieved using commercially available cyclic DACs. Data collected showed that it was possible to achieve a wide variety of dense and porous membranes by using a single family of compounds.[35]



Scheme 36. Synthesis of non-commercial (methoxy ethyl) carbonates as solvents for PVDF membrane preparation.[35]

PC and diphenyl carbonate (DPC) were instead employed as diluents to prepare PVDF hollow fibre membranes through a triple-orifice spinneret in thermally induced phase separation (TIPS). In TIPS techniques, polymer precipitation is caused by a decrease in temperature which can occur steadily or abruptly by immersion in a coagulation bath.[226] The concentration of DPC and PC generated different membrane structures showing significant effects on the permeability, rejection, and mechanical strength of the membrane.[240] In particular, PC provided all the membranes a porous inner and outer surface (*ca* 45% porosity and 5.5 μm average pore size) while dense structures were detected in the absence of PC.[241] The PVDF membrane mechanical strength remained unchanged because of the negligible impact of the solvents used as the bore liquids on the membrane bulk structure.[241] Similarly, PC was used as co-extrusion solvent at the outer layer of a PVDF dope solution in a TIPS process, leading to significant improvements in membrane's pure water permeability stability.[242] The penetration of the PC inside the membrane considerably changed the surface and sublayer structure.

In addition, the effects of solvents and temperature on the crystal formation were investigated for vinylidene fluoride/trifluoroethylene copolymer P(VDF-TrFE). Highly crystalline vinylidene fluoride/trifluoroethylene copolymer P(VDF-TrFE) thin films were fabricated by spin casting using DEC as polar solvent.[243]

7.2 Polylactic acid membranes

DMC can be also employed for the preparation of different type of polylactic acid (PLA) membranes such as:

- PLA fibres via Solution Blow Spinning (SBS), a technique which allows to produce micro- and nano-scale fibres from polymeric solutions through pressurized air using a specialized nozzle;[244]
- PLA porous bioactive nanofibers through SBS combined with thermally induced phase separation;[245]

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- Electrospun nanofibrous supports made of PLA and gelatin.[246] The support was then used for the production of green Thin-Film Composite (TFC) membranes, which can offer a sustainable solution for the separation of complex mixtures in aqueous and Organic Solvent Nanofiltration (OSN).[246] The electrospinning of PLA from DMC solutions produced ultrafine nanofibers in the presence of the ammonium salt additive.[246]

PLA was also used in combination with bamboo fibre in the presence of DMC to produce a bio-based membrane applicable as membrane backing material. The biobased membrane supports exhibited a porous structure (porosity of 0.719 ± 0.132) with tensile strengths (32.7−73.3 MPa) comparable to conventional materials, such as polypropylene. The synthetized supports were found to be stable in green polar aprotic solvents including Cyrene, 2-Me-THF, γ-valerolactone, and PC.[247]

The production of poly(glycolic-co-lactic acid) (PLGA) and poly(ε-caprolactone) microspheres were obtained under ambient conditions using one-step electrohydrodynamic jetting (atomisation) and TIPS in DMC. The presence of DMC generated microspheres with a diameter range of 150–300 μm, suitable for use in a minimally invasive, in situ forming scaffolds.[248]

7.3 Polyamide membranes

Another example of OCs as green solvents in membrane preparation was presented by Shi and co-workers, in which DMC and tannic acid (TA) were used to prepare high performance polyamide (PA) Reverse Osmosis (RO) membranes. RO membranes are used to separate low molecular weight solutes, i.e., inorganic salts or small organic molecules from a solvent. For this reason, these membranes find applications in the purification of water (desalination), as concentration step in the food industry (concentration of fruit juice, sugar, coffee), and the dairy industry (concentration of milk prior to cheese manufacture).[239]

The characterization of membrane achieved from TA showed that the presence of DMC changed the membrane structure, creating a more pronounced leaf-like architecture, thus demonstrating the significant contribution of the solvent in the final membrane morphology and characteristics. TA and DMC endowed the RO membranes with a high flux and a high salt rejection (99.03 ± 0.02%).[249] DMC can also be used as co-solvent to modify the interfacial polymerization (IP) process of polyamide membranes. DMC-modified membrane rejection improved while maintaining an excellent flux.[250]

In addition, DMC promoted the miscibility of aqueous and organic phases, thus enhancing the diffusion rate of m-phenylenediamine (MPD) from the aqueous phase into the organic phase. The accelerated diffusion of MPD due to DMC affected the RO membrane structures and performance i.e., increasing the overall thickness of skin layer.[249]

7.4 Polycarbonate membranes

Poly(trimethylene carbonate)-dimethylamine (PTMC-dMA) porous membrane-based scaffolds were produced via air-water interfacial phase separation using PC as swelling agent. The formed membrane could find possible applications in tissue engineering.[251]

7.5 Cellulose acetate membranes

The formation of cellulose acetate nanofibers via electrospinning was performed using DMC and cyclopentanone (CPO) as solvent system. The solvent composition affected the fibre diameter, morphology and porosity. DMC, due to its higher volatility, was responsible for pore formation.[252]

7.6 Ion-exchange membranes

Ion exchange membranes made of highly porous polytriazole and containing sulfonic acid functionalization were prepared by solution casting followed by immersion in a non-solvent bath and applied for selective protein adsorption using a mixture of 1-ethyl-3-methylimidazolium acetate ([C_2mim]OAc) and DMC as media.[253] These type of membranes may be useful for protein separation and purification, offering higher flow rates compared to chromatographic techniques, thus reducing the processing time.[253]

7.7 Ionomer membranes

EC was used in combination with sulfolane (SL) as a plasticizer to produce lithiated Nafion ionomer membranes, applicable both as electrolyte and separator. The conductivity of these membranes saturated with EC/SL is promising for various practical applications like the use as a polymer electrolyte in developing a new generation of lithium-ion batteries with enhanced safety.[254]

7.8 Poly(hydroxybutyrate- based membranes

Papchenko et al. compared several solvents for the casting of a poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) random copolymer-based membrane with potential applications in gas separation and CO_2 capture.[255] Among them, DMC allowed the production of polymer films with transport properties similar to those obtained with chloroform, and it also led to stable crystallinity of the samples over time.[255] These results render DMC a green alternative to $CHCl_3$ without compromising the separation performance.[255]

8. Organic carbonates in materials and nanoparticles preparation

OCs have shown interesting proprieties as polar media for the preparation of materials and nanoparticles in substitution of DMF, NMP and DMSO.[256]

DMC was employed as solvent for the fabrication of 3D porous PLGA-biomimetic carbonated apatite composite scaffolds[257], for the Liquid Phase Exfoliation (LPE) of pristine biochars as a substitute of NMP,[258] in the production of porous alumina ceramics[259] and in the debinding assistance of stereolithography-based 3D-printed alumina green bodies.[260] These latter materials subsequently underwent thermal debinding and sintering to obtain alumina ceramics. DMC

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application in this process showed to positively affect the microstructure and properties of 3D-printed alumina ceramics.[260] The obtained materials could be used as ceramic cores for hollow blades in aircraft engines.[260]

DMC, DEC and EMC find application as anti-solvents to improve the efficiency of quasi-two-dimensional (quasi-2D) perovskites[260] and perovskites solar cells (PSCs).[261,262] The former compounds have been identified as promising emitters for high-efficiency blue PeLEDs. In particular, the residual DMC in the perovskite can impede the grain coarsening during the heating process and preserve smaller grain size than that of the commonly used anti-solvent, chloroform. Furthermore, a better miscibility with the precursor solvent (DMSO) and a higher boiling point benefit a more homogeneous morphology.[263] Additionally, DMC solvent molecules have been shown to act as template in the production of methylammonium ($CH_3NH_3^+$ or MA)-based 2D Ruddlesden-Popper perovskites.[264]

The combination of PC as binder and DMC as solvent was employed for the development of an ultra-low-temperature co-fireable Li_2WO_4 substrate through tape-casting technique. The sintered substrate displayed a relatively high thermal expansion coefficient (*ca* 16 ppm/°C) and excellent microwave dielectric properties with a relative permittivity of 5.4 and a very low dielectric loss of 9.21×10^{-5} at 5 GHz, rendering it suitable for microelectronic applications.[265]

Grafting organic functionalities on inorganic supports is one of the most used methods for their preparation. While toluene usually is the solvent of choice for the grafting reaction, it can be substituted with greener media i.e., (+)-α-pinene, (−)-β-pinene, DMC, (+)-limonene, and Me-THF, even if only in the latter case no residual solvent molecules could be detected.[266]

Highly porous biocompatible composites made of polycaprolactone (PCL) and 45S5 Bioglass (BG) were prepared by a Solid–Liquid Phase Separation Method (SLPS) using either DMC or dioxane as solvent. Mechanical properties of the resulting composite showed a dependence also on the kind of solvent used for preparation. Composites prepared with dioxane showed enhanced stress at deformation and higher elastic modulus with respect to those prepared with DMC. [267]

Mixtures of castor oil (CO) and DMC were used as media in a microfluidic-assisted solvent extraction process resulting in the formation of hollow silica microspheres with a hole on the surface with potential application as catalyst supports, microreactors or as capturers for cells.[268] Increasing the DMC content led to formation of filbert-like silica solid microspheres instead.[268]

PCL electrospun structures for tissue engineering were prepared using a combination of glacial acetic acid as solvent and EC as a co-solvent. EC concentration in the mixture was able to influence the ultrafine PCL fibre diameter, which decreased as EC concentration was increased. Therefore, this stable and low toxic solution electrospinning system, may provide a valid strategy in tissue engineering field.[269]

EC was also used to dissolve low molecular weight methacrylate end-functionalized polymers i.e., poly(trimethylene carbonate-dimethacrylate), poly(D,Llactide-dimethacrylate), and poly(ethylene glycol-dimethacrylate) to produce porous crosslinked polymer networks applicable in the biomedical field.[270]

EC, PC and GC showed to be optimal for the repulsive osmotic delamination of 2D materials as an alternative to N-methylformamide, N-methylacetamide.[271] This technique is useful to achieve delamination into monolayers of ionic-layered compounds with quantitative yield.[271]

Concerning nanomaterials production, ruthenium nanoparticles can be deposited on thermally reduced graphite oxide using PC. These Ru@graphene nanomaterials are active catalysts for the solvent-free hydrogenation of benzene to cyclohexane under mild conditions (100 °C, 10 bar) with activities of 34,000 (mol cyclohexane)·(mol Ru)$^{-1}$·(h^{-1}) and over 90% conversion in at least ten consecutive runs.[272] Additionally, esterified cellulose nanocrystals could be obtained by solution blow spinning (SBS) using DMC as solvent.[273]

Finally, two-dimensional titanium carbide (Ti_3C_2Tx) MXene was effectively dispersed in PC, expanding the opportunities for processing techniques, such as mixing MXenes with other nanomaterials or polymers to form composites, preparing inks for printing.[256]

GC can be used as a suitable green solvent for the synthesis of metal–organic frameworks (MOFs). In particular, Itatani and co-workers reported the synthesis of a zinc-based zeolitic imidazolate framework-8 (ZIF-8) using GC, which could then be recycled and reused for several cycles.[274]

9. Organic carbonates in surface modification

The enhanced molecular transport together with the good dissolution proprieties of PC, renders it a suitable solvent for the preparation of alcohol-based monolayers on the surfaces of silicon oxides.[275] Monolayers prepared from alcohol-based reagents have been previously introduced as an alternative approach to covalently modify the surfaces of silicon oxides. This strategy can be utilized to create silicon oxide surfaces with hydrophobic, oleophobic, or charged functionalities.[275] In a similar fashion, surface modification of smectites can be performed using five-membered cyclic OCs, i.e., GC, 4-(2-hydroxyethyl)-1,3-dioxolan-2-one (HED), 4-(4-hydroxybutyl)-1,3-dioxolan-2-one (HBD), 4-((benzyloxy)methyl)-1,3-dioxolan-2-one (BMD), and 4′-(oxybis(methylene))bis(1,3-dioxolan-2-one) (OMD) and hexahydrobenzo[d][1,3]dioxol-2-one (HDD) as media (Figure 4).[79]

DMC and EC-PC mixtures were found to be promising solvents for the adsorption of the dye Bixin onto acid- and alkali-treated kaolinite[276] and for the adsorption of triblock Pluronic surfactants bearing poly(ethylene oxide) (PEO) chains of different lengths, on silica.[277]

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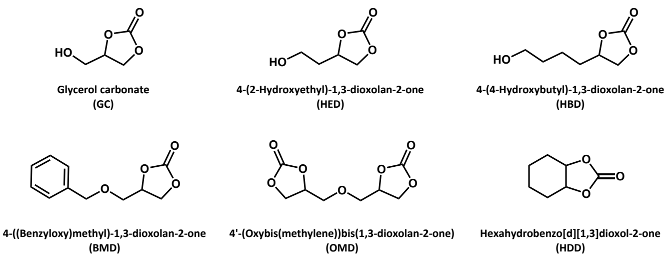

Figure 4. Cyclic OCs employed as media for the surface modification of smectites.

10. Organic carbonates as extracting solvents

Several examples of OCs employed as extracting solvents in a wide variety of applications are available in the literature; examples include liquefaction processes, compounds recovery and uses for the determination of pollutants. In this latter case, Dispersive Liquid–Liquid Microextraction (DLLME) for the determination of lead content in water can be performed using DMC as extraction solvent.[278] The analysis of DMC extracts can be also used for the determination of Volatile Fatty Acids (VFAs) concentration in digestates.[279] In addition, DEC in combination with ionic liquids showed enhanced performances for the determination of metallic impurities in *Arnica montana L.* infusions via DLLME.[280] DEC can be also used as extractant for the analysis of highly substituted hydrophobic chlorophenols in wines using Liquid-Phase Microextraction (LPME) and Capillary Electrophoresis (CE).[281]

10.1 Organic carbonates in liquefaction processes

Pinewood shaves can be liquefied using PC and GC in substitution of 2-ethylhexanol with a biomass conversion of 96%, 98% and 71%, respectively. The bio-oils obtained led to significantly better calorific properties than those from the biomass itself.[282] Liquefaction of recycled newspaper, instead, can be carried out in the presence of polyhydric alcohols and EC under acidic conditions.[283]

10.2 Organic carbonates in the extractions of oils and fatty acids

DMC was employed in the extraction of diglycerides (DAGs) and free fatty acids (FFAs) from salmon oil[284] and of kernel oils from *litsea cubeba* (LC).[285] In this latter case, DMC displayed enhanced performances compared to alcoholic solvents (yield values *ca* 96%) and with values similar to n-hexane (*ca* 96% yield). In addition, micronutrients in oils extracted by these green solvents were quantified much higher than that extracted by *n*-hexane.[285] DMC can also be employed as kernel oil extracting solvent through a controllable blender extractor (CBE).[286]

The application of DMC and DMC-EtOH mixtures as solvents in the Pressurized Liquid Extraction (PLE) of crambe seed oil showed greater oil removal from the seeds under pressurized conditions.[287,288]

Tommasi and co-workers developed a new lipid extraction protocol for obtaining a fatty-acids-rich extract from the diatom *Phaeodactylum tricornutum*.[289] Choline chloride-based deep eutectic solvents (DESs) and microwaves (MWs) pretreatments combined with DMC and $scCO_2$ as extraction solvents allowed to increase both the selectivity and the total fatty acid (TFA) extraction yield of DMC. In particular, TFA yield and fatty acid profile resulted comparable to those of the traditional Bligh and Dyer extraction method[290] with a much better selectivity (88% vs 35%). This pretreatment was also demonstrated to significantly improve the extraction efficiency of $scCO_2$, increasing the TFA yield by a factor of 20 and providing highly purified triglyceride extracts.[289] In addition, milk fat extraction can be performed from ghee residue using DMC as solvent.[291]

An Ultrasonic-Microwave-Assisted Extraction (UMAE) method with DMC was developed for the extraction of Manchurian walnut kernel oil (MWKO) with a maximum extraction yield of 59%.[292]

10.3 Organic carbonates for compounds recovery

EC, PC and DMC showed to be suitable media for the recovery of polyhydroxybutyrate (PHB), biosynthesized poly(3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV)[293] and polyhydroxyalkanoates (PHA) from municipal waste activated sludge.[294–296] The same solvents can be used to recover PHA from bacterial cytoplasm, i.e., *Cupriavidus necator* cells[297–299], genetically modified *E. coli* cell cultures[300] as well as from mixed microbial cultures.[301–304] With genetically modified *E. coli* cell cultures, PHB yield values from DMC-based extraction were similar to or higher than those achieved by using chloroform (≥ 67%).[300] Particularly, EC-assisted PHB extraction from *Cupriavidus necator* cells was obtained with a recovery percentage of 98% and product purity up to 98% which was the highest among the other solvents tested (DMSO, DMF, hexane, propanol, methanol, and acetic acid).[298]

EC was also tested for the industrial separation of acetone and diisopropyl ether employing extractive distillation, even if DL-limonene showed higher performances.[305]

Acidified GC and EC can be useful for the pretreatment of sugarcane bagasse with a glucose yield of 80% and 15%, respectively.[306] The usage of GC is preferred also because its decomposition produces glycerol while EC generates EG which is generally harmful.[307]

PC was found to be a suitable solvent for the isolation of PO during propylene epoxidation[308] and for the extraction of aromatics in naphtha.[309–312] Specifically, a mixture of PC and diethylene glycol as solvent system led to an increase in the utilization efficiency of naphtha[312] while DMC/*n*-butyl acetate mixtures were used as extracting media for the separation of coal gasification tar residue (CGTR).[313] PC and BC were also used for the extraction of artemisinin from *A.annua* with high efficiency (90-95%).[314]

DMC could be also used to extract β-carotene from *Rhodotorula glutinis* yeast,[315] 6-methoxypodophyllotoxin from *Linum* tissues via ultrasound-assisted extraction[316] and peroxidase from bitter gourd (*Momordica charantia*); the latter one via a three-phases partitioning technique, yielding a peroxidase recovery and fold purity of 177% and 4.84, respectively.[317]

DMC-based binary azeotropic mixtures showed good performances according to a computer-aided product design in extracting volatile aroma molecules widely used in perfume and cosmetic industries, i.e., α-pinene, DL-Limonene, α-terpinene, terpinolene and many more.[318]

DMC finds applications as extracting media for the biomonitoring of nicotine in aqueous samples[319] and it can be employed as precipitating agent to isolate lignin from rice straws with 89% purity after a fractionation step.[320]

Finally, a three-phases partitioning system with DMC as organic phase and sodium citrate as salt phase was used for partitioning of exopolysaccharide (EPS), namely, EPS-D, from fermentation broth of *Phellinus baumii*. This procedure may be applied also for efficient partitioning of natural biomolecules.[321]

DEC was positively tested as possible entrainer for separating 1-hexene and *n*-hexane by extractive distillation[322] as well as a green extraction solvent for gold(III) recovery from copper-rich sources[323] and chlorophenol determination in water samples with dispersive liquid–liquid microextraction.[324] On this latter application, DEC can be employed as a substitute instead of more toxic or hazardous solvents i.e., hexane, chloroform, toluene and diethyl ether.[324]

In addition, DEC can be employed as solvent for the determination of polycyclic aromatic hydrocarbons (PAHs) in different environmental matrices through GC–MS.[325]

Mixtures of water, propionic acid and DEC can be used for the recovery of propionic acid from aqueous solutions, i.e., fermentation broth and wastewaters.[326]

11. Organic carbonates in Analytical chemistry

DMC as well as mixtures of PC and ethanol were effectively employed as eluent phase in Inductively Coupled Plasma Mass Spectrometry (ICPMS)[327], HPLC[328] and liquid chromatography,[329] respectively. Mixtures of PC and ethanol may be considered a greener approach for pharmaceutical applications in substitution of CH_3CN. Such a replacement is achievable without any major compromise in terms of elution order, chromatographic retention, efficiency and peak symmetry even if, due to a reduced mass transfer of analytes in PC based mobile phases, optimal flow rates (necessary for reaching maximum of efficiency) are lower compared to CH_3CN-based mobile phases.[329] Concerning ICPMS applications instead, the employment of DMC may facilitate the elution and detection of novel hydrophobic compounds and improve column recovery under standard ICPMS conditions and instrumental set-up without a compromise in detection limits.[327]

An assay method incorporating PC as solvent was also developed to determine Chlorthalidone (CLD) and Cilnidipine (CIL) in bulk and tablet dosage form using four different UV spectrophotometric methods. Due to the solubility of most drugs in PC, this method can be adapted for the analysis of CIL and CLD drugs and it can be adopted by the Quality Control department for regular research and sustainable development.[330]

In another example, the addition of supercharging reagents, i.e., PC, EC and BC in Electrospray Ionization Coupled Mass Spectrometry (ESI-MS) has demonstrated to increase the protein ion charge as well as narrowing protein charge-state distributions without impacting the obtained drug-to-antibody (DAR) values.[331–333] Particularly, 5% (v/v) concentrations of BC and 4-vinyl-1,3-dioxolan-2-one can be added to ESI solutions to form higher charge states of cytochrome c and myoglobin ions than by using more traditional additives i.e., sulfolane, or *m*-nitrobenzyl alcohol.[332]

DMC was also used as eluent for the chromatographic purification of a 10-aminoacid-long peptide (purity of 98.5 %)[334] and for the separation of two small molecules i.e., caffeine and paracetamol.[335] Results indicated that a small amount (7 % v/v) of DMC has the same efficiency as a 2.5-times larger CH_3CN volume (18% v/v), and larger efficiency than alcohols i.e., ethanol and isopropanol in small molecule separation.[335]

12. Organic carbonates in biological/biochemical applications

Linear and cyclic OCs found some interesting applications as media in biochemical processes and assays. EC showed to be an appealing alternative to formamide and formaldehyde in Fluorescence *In-Situ* Hybridization (FISH) designed for double-stranded DNA probes in plants. Adding EC to the hybridization solution not only allowed successful overnight hybridization but also gave a possibility to reduce the hybridization time. The method was reproducible in all DNA of the plants studied (*Allium, Nigella, Tradescantia, Vicia*) giving a positive stimulus for improving gene-mapping approaches in plants.[336]

PC was employed as media for a colorimetric pyrophosphate assay, used for the determination of the $P_2O_7^{4-}$ anionic species (PPi) and based on the formation and reduction of the 18-molybdopyrophosphate ($[(P_2O_7)Mo_{18}O_{54}]^{4-}$) anion. This process decreased the interference by ATP and prevented a yellow coloration of the reducing agent (ascorbic acid) due to excess Mo(VI) species. Thus, this method showed to be useful for the assay of AMP+PPi forming enzymes, including adenylation enzymes.[337]

Solvent systems composed by isosorbide dimethyl ether and PC (also with DMSO in some cases) were used to prepare oral non-steroidal anti-inflammatory drugs (NSAIDs). These compounds find applications in the management of inflammatory diseases, including arthritis, bursitis and tendonitis.[338] On this topic, PC and other moderately hydrophobic solvents in combination with phase sensitive polymers can be utilized for modifying drug release from injectable implant systems for 21 days.[339]

Finally, enzyme-catalysed transesterification of ethyl butyrate with *n*-butanol[340,341] and microalgae biomass (*Scenedesmus sp*) to produce bioethanol and biodiesel[342] was performed using GC and DMC as solvent, respectively.

12.1 Solid phase peptide synthesis (SPPS)

Researches focused on the development of greener protocols for the production of pharmaceutical grade peptides via Solid

Phase Peptide Synthesis (SPPS) by introducing more sustainable alternatives to the most common reagents and solvents.[343] On this topic, Ferrazzano and co-workers demonstrated that the traditional DMF-based protocol for industrial fluorenylmethoxycarbonyl (Fmoc) SPPS could be replaced by a greener one by using combinations of Cyrene, sulfolane, or anisole with DMC or DEC, in different proportions.[344] This method showed applicability on a wide range of oligopeptides, i.e., Aib-enkephalin and Aib-ACP. Finally, this procedure was applied to the synthesis of the reduced form of the active pharmaceutical ingredient (API) Octreotide isolating it in comparable yield and purity compared to that obtained with DMF.[344]

Also, the deprotection of the Fmoc groups can be performed in a sustainable way by employing 3-(diethylamino)propylamine (DEAPA) as an alternative to piperidine in N-octyl pyrrolidone/DMC 8:2 v/v solvent system. DMC allowed a decrease in solvent viscosity, making the mixture suitable for the automated solid-phase protocol.[345] This approach was proved to be able to minimize the formation of side products while achieving comparable results to those obtained with piperidine.[343]

13. Organic carbonates in cultural heritage

Several investigations aimed to replace toxic solvents with greener ones in different aspects of cultural heritage preservation and restoration i.e., old varnishes, paints and tapes removal.[346]

For instance, the cleaning of wax-based coatings applied on indoor 1460s bronzes was performed with a gel made by PHB as thickening agent, biodiesel and DMC. DMC acts as a solubilizing agent for PHB, forming a jelly phase. This gel was then applied for the removal of fresh and aged beeswax coatings, avoiding problems related to solvent residues and ensuring safety for the artworks, the operators and the environment.[347] Polymeric gels poly(ethylmethacrylate)-diethylcarbonate (PEMA-DEC), are also able to remove pressure sensitive tapes (PST) components without damaging the painting underneath.[348,349]

Graffiti and murals removal from historic building, masonries and stone artworks can be achieved with a series of two-component systems which combines silica sol-gel chemistry and DMC as green solvent to be loaded into the gel. The efficiency of this system in adsorbing/trapping commercial red aerosol spray paint from Istrian stones was investigated, showing to be a promising cleaning agent.[350] Moreover, DMC was also studied as swelling solvent to produce thiol-ene photocured organogels by combining five different thiol or allyl functionalized bio-based monomers, namely isosorbide, pyrogallol, and limonene. DMC swollen gels were found to be effective in removing the varnish from the surface of the artwork while avoiding adhesion to the surface layer of the paintings [351] while DMC alone was employed for the removal of thermally aged oil-painted mock-ups.[352]

A ternary mixture of water, PC and C9-11E6 (a non-ionic alcohol ethoxylate surfactant) was employed for the dewetting of a methacrylate/acrylate co-polymer film. The surfactant favours the loss of adhesion of the polymer which may be found on works of art because of previous restoration interventions, which needs to be removed.[353]

PC was also employed as green media in magnetic nano gel microemulsions, providing a drastic improvement in the cleaning efficiency of archaeological cartonnage.[354]

Finally, PC, DMC, DEC and DBC were used in combination with a biodegradable non-ionic surfactant in water to formulate a novel nanostructured cleaning system. This system was loaded in highly retentive hydrogels and effectively applied in the selective removal of over-paintings from laboratory mock-ups and from real pieces of street art.[355]

14. Organic carbonates as cleaning co-solvents

OCs demonstrated to be excellent co-solvents as cleaning and de-painting products for carpets, rugs, and fabrics. PC can be used as a sequestering agent in environmentally benign cleaning formulations.[356] In high concentrations (up to 25%), PC can be employed as solvent for cleaning processes which involve human contact.[357] With its softening and swelling effect on paint, PC turned out to be an appropriate solvent in aqueous mixtures for the removal of paints from skin. In this application it was added as co-solvent in up to 40%.[358]

The U.S. EPA evaluated the use of PC as solvent in de-painting operations in air logistics centres.[359] Furthermore, alkylene carbonates can be used to reduce the odor of amine-containing compounds like urine. An advantage is the high biodegradability of OCs. Therefore, odor reducing agents containing EC, PC or BC can be applied in environmental open places like zoos, wool plants, and fish canneries.[360] Reduction of odor is achieved by reaction of the respective carbonate with the amine. Furthermore, DACs like GC are starting materials to synthesize non-ionic surfactants which can be used in cleaning products.[361]

15. Organic carbonates in cosmetics and as sunscreen

Examples of DACs displaying long alkyl chains employed in cosmetics can be found in literature; most of them are reported in patented formulations.

Natural make-up primers were prepared using dioctyl carbonate (DOC) as oil phase solvent in which plant and mineral derived compounds are dissolved into.[362] DOC was applied as emollient in anhydrous cosmetic sunscreens together with diisopropyl sebacate, isononyl isononanoate and diisopropyl adipate, an UV filter system and silicone blends (selected from the group of dimethicone, dimethicone/vinyl dimethicone co-polymer and polydimethyl siloxane). The obtained cosmetic sunscreen displayed enhanced stability, provided a high sun protection factor (SPF).[363] Emollients impact (namely, alkyl benzoate, dibutyl adipate, caprylic/capric triglyceride, coco-caprylate, isopropyl myristate and dioctyl carbonate) on the UV-filter performances showed nearly no influence on the SPF and on the UVB protection while the UVA shielding decreased with

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the decrease in the emollient polarity (dicapryl carbonate being the least polar). Therefore, polar emollients are advocated to optimize the UVA protection.[364,365]

16. Organic carbonates in Varnish and Paints

OCs can be used for nonaqueous liquid pigment dispersion due to their high boiling and flash points.[366] Usually, 50-75 mass% of the chemicals in the Lacquer wire-coating process are organic solvents. In particular, thin wires need a higher amount of organic solvents. In addition, cresol could be replaced by PC after comparison of the complete life cycle of both solvents including production, application, and waste removal in the copper wire-coating process.[367]

Opportunely modified OCs have been employed in new water-based varnish formulations.[368] Among the OCs tested 2-(2-methoxyethoxy)ethyl methyl carbonate (DGlyMC) resulted the best one also in terms of toxicological evaluation.[368]

17. Organic carbonates in Coatings

Miller et al. investigated the use of paint blends thinned by mixtures of DMC and tert-butylbenzene to create low-stress films to be used as solar absorber coatings. These coatings exhibited strong optical performance (FOM) with figure of merit and solar absorbance values of 91% and 97%, making them ideal coatings for next generation concentrated solar power plants.[369] Utilization of these solvents also helps reducing the paint's environmental impact, specifically by decreasing the VOC content and MIR value to 395 g/L and 1.04, respectively.[369]

PC was also tested for solution-processable deposition of CuSCN as hole transport layer (HTL) in bulk heterojunction solar cells despite with lower efficiencies compared to DMF and DMSO (2.5%, 4.5% and 4.2%, respectively).[370]

18. Organic carbonates in oil and natural gas processing industry

The FLUOR process is one of the oldest industrial applications of OCs (especially PC). This process uses PC as a physical solvent to remove CO_2 and H_2S. PC also removes C_{2+} hydrocarbons, COS, SO_2, CS_2, and H_2O from the natural gas stream.[371] In fact, PC has an equilibrium capacity for absorbing carbon dioxide several times higher than water and does not absorb high amounts of natural gas and hydrogen. With its low viscosity, low vapor pressure, and noncorrosive behaviour it is an excellent choice as an absorbing solvent.[372]

Other cyclic OCs, namely EC, PC, BC, hexylene carbonate (HexC), cyclohexene carbonate (CHexC), styrene carbonate (SC), GC and (chloromethyl)ethylene carbonate (CEC) were applied in substitution of sulfolane to mitigate residual aromatic content (dearomatization, desulfurization and denitrogenation) in liquid fuels.[373] Among them PC, EC, BC and SC showed competitive results compared to sulfolane, with PC providing promising process performance at a very competitive solvent to feed (S/F) ratio and specific energy consumption.[373]

19. Organic carbonates and Electronics

PC can be used as solvent in the formation process of alignment films for the development of liquid crystal devices. It is necessary that the solvent can be modified by a second solvent to control the surface tension during the process.[374] It turned out that PC can be used in both functions, with the best results obtained in combination with glycol ethers. Organic carbonates can be also used for sensors, i.e., a PC-based ammonia sensor was developed.[375]

Furthermore, PC was demonstrated to be an excellent solvent for capillary electrophoresis for the investigation of mobility and ionization constants of various aliphatic amines.[376] This technique allows to separate ionic compounds on the basis of their electrophoretic mobility, which in turn is dependent on the charge, viscosity and radius of the ions involved.[377]

Detection of thallium(III) and other inorganic salts has been accomplished by polarographic methods in PC as part of extractive mixtures with water[378] for 'salting-out' extractions.[379] Finally, neutral substances like phenanthrene could be separated by nonaqueous capillary electrophoresis using cationic additives in PC.[380]

20. Organic carbonates as electrolytes

20.1 Organic carbonates in lithium batteries

The development of rechargeable lithium batteries based on electrolyte solvents is considered a milestone in the field of energy storage and supply for electrical and electronic devices (Figure 5).[381,382]

The role of electrolytes in batteries is to serve as the medium for the transfer of charges, which are in the form of ions, between a pair of electrodes.

In lithium-ion batteries, lithium ions are solvated by an organic solvent and they diffuse freely between the two half-cells (anode and cathode compartments), which are physically isolated from each other by a separator membrane.[383–385] Thus, an ideal electrolyte solvent must have a high dielectric constant to dissolve high electrolyte salts concentration, have low viscosity to facilitate ion transport, be chemically inert to all cell components to improve battery lifetime, be liquid over a wide temperature range (i.e., have low melting point and high boiling point), and have low flammability (high flash point).[386]

PC is considered the preferred electrolyte in lithium battery due to a wide liquid range, high dielectric constant and static stability with lithium. Mixtures of EC and PC are considered the most suitable solvent system for common lithium salts to be used as the electrolyte liquid carrier in lithium-ion batteries[387–391] as well as EC and EMC blends,[392] thus representing a standard for the evaluation of new salts and electrochemical systems.[393–396]

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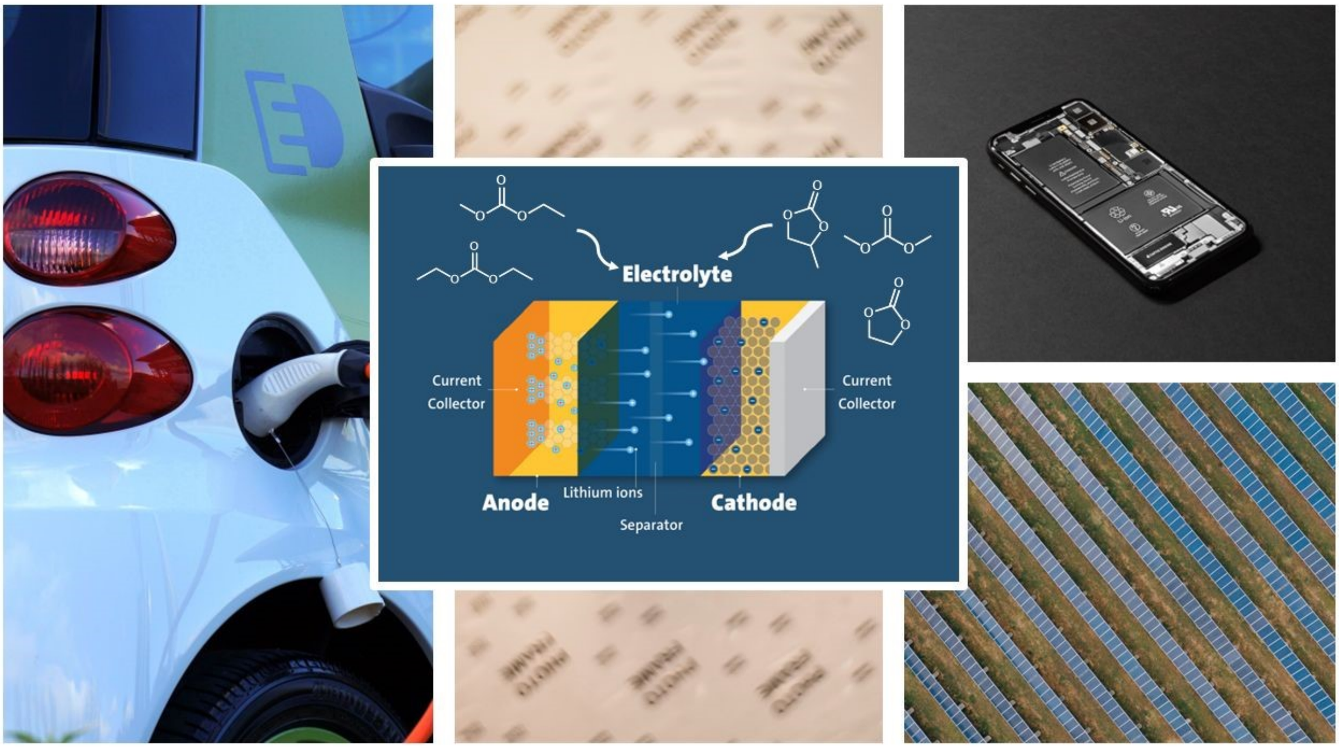

Figure 5. OCs as electrolytes in lithium-ion batteries.

On this matter, general investigations on the conductivity of organic electrolyte solutions were published by Petrowsky et al.[397] The mass transport and conductivity in DAC electrolytes (PC, EC, and DEC and mixture thereof) were determined for $LiClO_4$,[398] KPF_6 and $LiPF_6$,[399] and for LiBr in mixtures with iodine.[400]

EC and PC can be also combined with other compounds, i.e., lithium (fluorosulfonyl) (trifluoromethanesulfonyl) imide (LiFTFSI) and lithium bis(fluorosulfonyl)imide (LiFSI) to improve the stability and safety of Li-ion batteries[401–403] or with Deep Eutectic Solvents (DES) - choline chloride/ethylene glycol or choline chloride/malonic acid - to improve the thermodynamic and transport proprieties of $LiNO_3$.[404]

In addition, DMC is finding increasing application as a non-aqueous electrolyte component in the field of lithium rechargeable batteries, as attested by the number of patents in the area.[33,62,405] Hybrid aqueous-DMC electrolytes were also reported.[406]

Moreover, GC has a higher dielectric constant compared to other carbonate solvents used in lithium cell electrolytes. This enables larger quantities of Li salts, i.e., $LiF_2BC_2O_4$, $LiPF_6$, $LiBF_4$ and/or $LiB(C_2O_4)_2$ to be dissolved in GC.[407]

Finally, non-polar electrolyte solvents such as DMC and EMC can be selectively extracted from spent Li-ion batteries using sub-critical or $scCO_2$, while the recovery of the polar EC seems to be more challenging.[408] However, through a low temperature thermal treatment process (<150 °C) also EC can be successfully recovered.[409]

20.2 Fluorinated organic carbonates as electrolytes

Fluorinated DACs - fluoroethylene carbonate (FEC),[410–413] monofluoroethyl methyl carbonate (F_1EMC), difluoroethyl methyl carbonate (F_2EMC), methyl (2,2,2-trifluoroethyl) carbonate (F_3EMC),[414,415] bis(2,2,2-trifluoroethyl) carbonate (BTFC),[416] trifluoropropylene carbonate (TFPC) and their mixtures[417] have been extensively studied as electrolytes. These compounds showed promising performances (i) as high-voltage electrolytes for Li-ion batteries,[418–420] (ii) for localized high concentration electrolytes (LHCE),[421] (iii) to make highly concentrated electrolyte solutions for Si nano-flake powder negative electrodes[422] and (iv) for enabling long-term operation of Li-metal batteries at low temperatures.[423]

FEC was also added to a classical electrolyte mixture of EC and EMC to improve the thermal properties of the solid electrolyte

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interphases (SEI).[424] FEC finds applications as co-solvent in sodium metal anodes (SMEs), sorting out the low reversibility of SMEs in carbonate-based electrolytes.[425]

Furthermore, better cathode performances were noted when vinylene carbonate (VC) was added to an electrolyte EC solution.[426–429]

One major problem for all organic solvent electrolytes is flammability. This problem can be overcome by adding F_3EMC[430–432] or tris(2-chloropropyl) phosphate[433] to the electrolyte, although this flame-retardant characteristic affects the viscosity and capacity ratio during discharge.[434] Other studies evaluated the use of fluorinated ionic liquids and DMC as a co-solvent.[435]

20.3 Organic carbonates as electrolytes in other applications

Cyclic DACs were employed as media in the electro-catalytic reduction of 1,3-dibromopropane (DB3) at metallic interfaces such as Au, Pt, Pd, and Rh.[436] This process permits both the dissolution of precious metals and their deposition onto glassy carbon and graphite, applicable for the fabrication of composite materials.[436] Moreover, SEI mechanical properties can be improved by polymer species generated from solvent decomposition, i.e., EC, PC, DEC, FEC and VC.[437–440]

VC is also shown to decrease the formation of potentially toxic organofluorophosphates (OFPs) within the electrolyte during cycling at conventional upper cut-off voltages (UCVs) while on the other hand triggering OFP formation at higher UCVs.[441] Moreover, VC finds application as filmogen to realize a stable solid-solid cyclic process in lithium-sulfur batteries (LSBs).[442]

EC/DEC blends, in the presence of potassium salts, allowed to achieve superior cycling stability and kinetics performance of the hard carbon (HC) anode in potassium-ion batteries (PIBs).[443]

EC has been shown to stabilize DEC by the weak intermolecular interactions, enhancing the energy difference between the orbitals of the $Li^+ (EC)_x(DEC)_y$ complex, demonstrating strong capability against reduction.[444] $LiPF_6$-methyl acetate/DEC solution systems can be applied as electrolytes in dual-ion batteries.[445] Dimethyl dicarbonate (DMDC)[446] as well as mixtures of DMC and co-solvents such as PC, 1,1,1,3,3-pentafluorobutane (PFB) and other fluorinated aromatic hydrocarbons have also been investigated.[447–449]

A colloid liquid electrolyte (CLE) can be designed using EC/DMC solvent system and trace amounts of lithium thiocarbonate (LTC) colloids. This combination showed to improve the Li^+ transfer kinetics at the cathode/electrolyte interface.[450]

Additionally, gel polymer electrolyte (GPE) and solid polymer electrolyte (SPE) technologies use organic carbonates in combination with Li salts to obtain high conductivity, cohesion and adhesion.[451,452] An effective lithium-air GPE system could be applied with a 50% epoxidized natural rubber polymer with 35% $LiCF_3SO_3$ and 10% PC as plasticizer. Employing different mixtures of EC or PC lower conductivities were observed.[453] In contrast to a liquid electrolyte system of 1.0 M $LiClO_4$/PC, the polymer electrolyte is more stable against corrosion.[454]

Moreover, non-commercial OCs i.e., bis(2-methoxyethyl) carbonate (Gly_2C)[455] and chlorinated EMC showed promise as electrolytes, exhibiting considerable oxidative/reductive stability, relatively weak solvation ability and low flammability.[456,457]

21. Other applications

In this section are reported other applications in which organic carbonates have been employed which were not discussed beforehand.

EC and PC were applied as solvents for the synthesis of dielectric gels with 2-ethylhexyl acrylate (2-EHA) and 4-acryloylmorpholine (ACMO) as polymer networks. The sensitivity of the capacitive sensor made of the new dielectric gel increase about 6 times compared to the sensors made of VHB, polydimethylsiloxane (PDMS), or Ecoflex making them suitable for its application as the transparent cover layer of a cell phone.[458]

PC, EC and GC can be added to peroxide solutions to improve their stability over an accelerated aging period. This result can be exploited to improve the stability of ready to use disinfectants regardless of the rest of the ingredients included in the formulations.[459]

Kupareva et al. investigated the removal of silicon and its chemical species from oil in alkaline conditions by adding DMC to the reaction mixture. DMC favoured the reduction of solid products in the reaction mixture, thus fostering the oil recycling process.[460] According to Okamoto et al.[461–463] the siloxane bond is efficiently cleaved with DMC over solid-base catalysts to afford methoxy-terminated linear siloxane and carbon dioxide.

Scanning Electrochemical Microscopy (SECM) used in the feedback mode is one of the most powerful versatile analytical tools used in the field of battery research. However, the application of SECM in the field of lithium-ion batteries (LIBs) faces challenges associated with the selection of a suitable redox mediator due to its high reactivity at low potentials at lithium metal or lithiated graphite electrodes. In this regard, the electrochemical/chemical stability of 2,5-di-tert-butyl-1,4-dimethoxybenzene (DBDMB) is evaluated and benchmarked with ferrocene. This investigation is systematically carried out in both linear and cyclic OCs of the electrolyte recipe. Measurements of the bulk current with a microelectrode proved that while DBDMB decomposes in EMC-containing electrolyte, bulk current remains stable in cyclic carbonates, EC and PC.

Ferrocene was studied as an alternative redox mediator, showing superior electrochemical performance in EMC-containing electrolytes in terms of degradation.[464]

Conclusions and future perspectives

As above stated, to the best of our knowledge, this is the first review focussing solely on the application of OCs as media. In this view we reported herein a comprehensive analysis on the applications of OCs as green solvents progressing from lab-scale to industrial applications.

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OCs are valued for their diverse physical and chemical properties, making them excellent alternatives not only in organic synthesis but also across a range of other applications. Research into the use of OCs as solvents has increased significantly over time (Figure 6), reflecting the growing recognition of their potential within a sustainability framework. According to the analysis on the type of OCs employed, numerous works are focused on the exploitation of commercially available DACs, i.e., DMC, EC and PC; however, many studies also focused on the development of custom-made OCs so to meet the specific chemical and physical criteria required for a precise transformation. This trend opens exciting possibilities for new applications, as these novel OCs can be synthesized in large quantities thanks to mature synthetic methods.

On the other hand, it should be mentioned that despite the well-documented low toxicity and hazardousness of most OCs, a comprehensive evaluation of the greenness of synthetic processes is still lacking. While tools like green metrics and life cycle assessments (LCA) are available, further research is needed on the end-of-life disposal and biodegradability of OCs to fully understand their environmental impact.

As highlighted in this review, OCs offer more than just a replacement for toxic solvents; they present an opportunity to revolutionize various scientific fields towards more sustainable practices. From improving battery performance and advancing materials science to driving innovations in green chemistry and enhancing industrial sustainability, their potential is vast. The widespread adoption of OCs as green solvents is likely to have far-reaching effects, making them a valuable resource for researchers and industries focused on developing more sustainable processes.

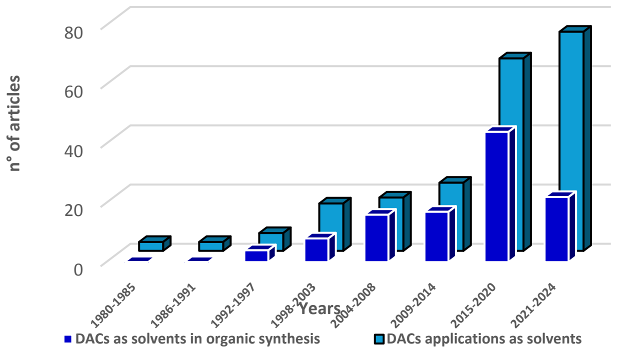

Figure 6. Number of scientific articles employing OCs as solvents in organic synthesis (light blue) and as media for different applications (dark blue). Articles in which OCs were used as media for polymerization and depolymerization reactions were considered as part of the organic synthesis group.

List of Abbreviations

[C_2mim]OAc	1-Ethyl-3-Methylimidazolium Acetate
2-EHA	2-Ethylhexyl Acrylate
2-Me-THF	2-Methyl-Tetrahydrofuran
2-Me-β-CD	2-O-Methylated Β-Cyclodextrin
4CzIPN	1,2,3,5-Tetrakis(Carbazol-9-Yl)-4,6-Dicyanobenzene
ACMO	4-Acryloylmorpholine
ADPS	3-((3-Aminopropyl)Dimethylammonio) Propane-1-Sulfonate
API	Active Pharmaceutical Ingredient
ATRP	Atom Transfer Radical Polymerization
BA	N-Butyl Acrylate
BC	Butylene Carbonate
BCB	4′-(Bromomethyl)-2-Cyanobiphenyl
BMD	4-((Benzyloxy)Methyl)-1,3-Dioxolan-2-One
BPO	Benzoyl Peroxide
BTF	Benzotrifluoride
BTFC	Bis(2,2,2-Trifluoroethyl) Carbonate
CAGR	Compound Annual Growth Rate
CBE	Controllable Blender Extractor
CE	Capillary Electrophoresis
CEC	(Chloromethyl)Ethylene Carbonate
CHexC	Cyclohexene Carbonate
CIL	Cilnidipine
CIR	Cosmetic Ingredient Review
CL	E-Caprolactone
CLD	Chlorthalidone
CLE	Colloid Liquid Electrolyte
CNTs	Carbon Nanotubes
CO	Castor Oil
CPME	Cyclopentyl Methyl Ether
CPO	Cyclopentanone
CPS	Chlorophosphonium Salt
CyO	Cyclooctene
DA15C5	Diaza-15-Crown-5
DAC	Dialkyl Carbonate
DAGs	Diglycerides
DAllC	Diallyl Carbonate
DAR	Drug-To-Antibody
DB3	1,3-Dibromopropane
DBC	Dibutyl Carbonate
DBDMB	Dimethoxybenzene
DCB	Dichlorobenzene
DCE	Dichloroethane
DCM	Dichloromethane
DEAPA	3-(Diethylamino)Propylamine
DEC	Diethyl carbonate
DEPG	Dimethyl Ethers Of Polyethylene Glycol
DES	Deep Eutectic Solvent
DETA	Diethylenetriamine
DGly$_2$C	Bis(2-(2-Methoxyethoxy)Ethyl) Carbonate
DGlyMC	2-(2-Methoxyethoxy)Ethyl Methyl Carbonate
DHMF	2,5-Bis(Hydroxymethyl)Furan
DLLME	Dispersive Liquid–Liquid Microextraction
DMA	Dimethyl Acetamide
DMC	Dimethyl Carbonate
DMDC	Dimethyl Dicarbonate
DMF	Dimethyl Formamide
DMI	Dimethyl Isosorbide
DMSO	Dimethyl Sulfoxide
DOC	Dioctyl Carbonate
DPC	Dipropyl Carbonate
DPhC	Diphenyl Carbonate
dppe	Bis(Diphenylphosphino)Ethane
EC	Ethylene Carbonate

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EG	Ethylene Glycol
EGD	European Green Deal
EMC	Ethyl Methyl Carbonate
EMIMBr	1-Ethyl-3-Methylimidazolium Bromide
EO	Ethylene Oxide
EPA	Environmental Protection Agency
EPS	Exopolysaccharide
ESI-MS	Electrospray Ionization Coupled Mass Spectrometry
FDA	Food and Drug Administration
F_1EMC	Monofluoroethyl Methyl Carbonate
F_2EMC	Difluoroethyl Methyl Carbonate
F_3EMC	Trifluoroethyl Methyl Carbonate
FEC	Fluoroethylene Carbonate
FFAs	Free Fatty Acids
FISH	Fluorescence In-Situ Hybridization
Fmoc	Fluorenylmethoxycarbonyl
FOM	Optical Performance
GC	Glycerol Carbonate
GCB	Glycerol Carbonate Butyrate
GCP	Glycerol Carbonate Propionate
Gly_2C	Bis(2-Methoxyethyl) Carbonate
GPE	Gel Polymer Electrolyte
GVL	Γ-Valerolactone
HBD	4-(4-Hydroxybutyl)-1,3-Dioxolan-2-One
HBpin	Pinacolborane
HC	Hard Carbon
HDD	Hexahydrobenzo[D][1,3]Dioxol-2-One
HED	4-(2-Hydroxyethyl)-1,3-Dioxolan-2-One
HexC	Hexylene Carbonate
HMF	5-Hydroxymethyl Furfural
HMTA	Hexamethylenetetramine
HR	Hardwood Residue
HTL	Hole Transport Layer
IBA	Isobutyraldehyde
iBuVE	Isobutyl Vinyl Ether
IBX	2-Iodoxybenzoic Acid
ICPMS	Inductively Coupled Plasma Mass Spectrometry
ILs	Ionic Liquids
ITO	Indium Tin Oxide
LC	*Litsea cubeba*
LEDs	Light Emitting Diodes
LHCE	Localized High Concentration Electrolytes
LIBs	Lithium-Ion Batteries
LiFSI	Lithium Bis(Fluorosulfonyl)Imide
LiFTFSI	Lithium (Fluorosulfonyl) (Trifluoromethanesulfonyl) Imide
LPE	Liquid Phase Exfoliation
LPME	Liquid-Phase Microextraction
LSBs	Lithium-Sulfur Batteries
LTC	Lithium Thiocarbonate
MBP	Methyl 2-Bromopropionate
MEA	2-Methoxy Ethyl Acrylate
MIAK	5-Methyl-2-Hexanone
MIBK	Methyl Isobutyl Ketone
MOF	Metal–Organic Framework
MPD	M-Phenylenediamine
MPS	Methyl Phenyl Sulfide
MTAE	Methyl-Tert-Amyl Ether
MTBE	Methyl Tert-Butyl Ether
MTO	Methyltrioxorhenium
MW	Microwave
MWKO	Manchurian Walnut Kernel Oil
NBA	N-Butylaniline
NBS	N-Bromosuccinimide
N-CNT	Nitrogen-Doped Carbon Nanotubes
NHC	Nickel-N-Heterocyclic Carbene
NIPS	Non-Solvent Induced Phase Separation
NMA	N-Methylaniline
NMA	N-Methylaniline
NMF	N-Methylformamide
NMP	N-Methyl Pyrrolidone
NSAIDs	Non-Steroidal Anti-Inflammatory Drugs
OBMF	5,5′-[Oxybis(Methylene)]Bis-2-Furfural
OC	Organic Carbonate
OFPs	Organofluorophosphates
OL	Organosolv Lignin
OMD	4′-(Oxybis(Methylene))Bis(1,3-Dioxolan-2-One)
OSN	Organic Solvent Nanofiltration
PA	Polyamide
PAHs	Polycyclic Aromatic Hydrocarbons
PAN	Polyacrylonitrile
PC	Propylene Carbonate
PCL	Polycaprolactone
PDMS	Polydimethylsiloxane
PDMS	Polydimethylsiloxane
PEDOT	Poly(3,4-Ethylenedioxythiophene)
PEF	Polyethylene furanoate
PEG	Polyethylene Glycol
PEMA-DEC	Poly(Ethylmethacrylate)-Diethylcarbonate
PEO	Poly(Ethylene Oxide)
PES	Polyethersulphone
PET	Polyethylene Terephthalate
PFB	Pentafluorobutane
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PHBV	Poly(Hydroxybutyrate-Co-Hydroxyvalerate)
PIBs	Potassium-Ion Batteries
PIPOx	Poly(2-Isopropyl-2-Oxazoline)
PLA	Polylactic Acid
PLE	Pressurized Liquid Extraction
PLGA	Poly(D,L-Lactide-Co-Glycolide)
PMDETA	Cubr/N,N,N0,N0,N00-Pentamethyldiethylenetriamine
PMDI	Poly4,4′-Diphenyl Methane Diisocyanate
PO	Propylene Oxide
PSCs	Perovskites Solar Cells
PST	Pressure Sensitive Tapes
PTC	Phase Transfer Catalysis
PTMC-dMA	Poly(Trimethylene Carbonate)-Dimethylamine
PU	Polyurethane
PV	Pervaporation
PVDF	Polyvinilydene Fluoride
RAFT/MADIX	Reversible Addition–Fragmentation Chain Transfer Polymerization/Macromolecular Design Via The Interchange Of Xanthates
RCM	Ring-Closing Metathesis
RO	Reverse Osmosis
SBS	Solution Blow Spinning
SC	Styrene Carbonate
scCO2	Supercritical CO_2
SECM	Scanning Electrochemical Microscopy
SEI	Solid Electrolyte Interphases

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SET-LRP	Single Electron Transfer Living Radical Polymerization
SFAME	Sunflower Fatty Acid Methyl Ester
SL	Sulfolane
SLPS	Solid–Liquid Phase Separation Method
SMEs	Sodium Metal Anodes
SPE	Solid Polymer Electrolyte
SPF	Sun Protection Factor
SPPS	Solid Phase Peptide Synthesis
TA	Tannic Acid
TDI	Toluene Diisocyanate
TEAB	Tetraethylammonium Bromide
TFA	Total Fatty Acid
TFC	Thin-Film Composite
TFE	Tetrafluoroethylene
TFPC	Trifluoropropylene Carbonate
TIPS	Thermally Induced Phase Separation
TMC	Trimethylene Carbonate
TO	Tin Oxide
UCVs	Upper Cut-Off Voltages
UMAE	Ultrasonic-Microwave-Assisted Extraction
VC	Vinylene Carbonate
VDF	Vinylidene Fluoride
VFAs	Volatile Fatty Acids
VIPS	Vapor Induced Phase Separation
VOS	Volatile Organic Solvents
ZIF	Zinc-Based Zeolitic Imidazolate Framework

Author contributions

G. Trapasso: Investigation, Data Curation, Visualization, Writing – original draft; F. Aricò: Conceptualization, Supervision, Writing – review and editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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Data availability Statement

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.