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Ring-opening Metathesis Polymerisation derived poly(dicyclopentadiene) based materials

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During the last two decades, poly(dicyclopentadiene) prepared by Ring-opening Metathesis Polymerisation has emerged as an important competitor for epoxy- and polyester resins. This review article summarises the contributions from academia in this timeframe. The fields of initiator system development, polymer chemistry and physics, composites of poly(dicyclopentadiene), use in self-healing composites, novel processing opportunities and macro- as well as microporous materials are covered.

1. Introduction

Dicyclopentadiene (DCPD)¹ is obtained as a by-product from steam cracking performed during the production of ethylene.^{2,3} DCPD finds applications in unsaturated polyester and hydrocarbon resins, in ethylene propylene diene monomer (EPDM) elastomers, as chemical feedstock, in cyclic olefin polymers and as a monomer for poly(dicyclopentadiene) (pDCPD) prepared

via Ring-opening Metathesis Polymerisation (ROMP). The worldwide DCPD market is estimated to exceed 500 million Euro in 2019 and is expected to grow by annually 5% over the next 5 years.⁴ Especially the market segment of highly purified DCPD is gaining growth rate as pDCPD increasingly finds applications. ROMP of DCPD results in a cross-linked polymer that possesses high notch-impact strength and offers high temperature and corrosion resistant properties as well as high stability *versus* chemicals. Furthermore, the polymer's surface is quickly oxidized in air and thus a relatively polar surface is generated which can be easily painted. An additional corona treatment or flaming as required for many other polymers is thus not necessary. ROMP-derived pDCPD is used for example in the manufacturing of agricultural equipment, of body panels, and of cells for the chlor-alkali industry or in the

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petrochemical industry for piping. Furthermore, reinforced pDCPD parts became accessible and enabled new concepts for construction designs. pDCPD is mainly processed *via* reaction injection moulding (RIM), resin transfer moulding (RTM) and vacuum-assisted RTM (VTRTM).^{5–10} By these techniques large and complex parts can be manufactured in a quick and efficient way. Its comparatively low density combined with good mechanical properties makes it environmentally beneficial for applications in the automotive domain, where fuel efficacy is an important topic. Lately pDCPD based technology has additionally targeted, amongst others, the markets of downhole tools, subsea insulation, circuit boards, pressure vessels and parts for the energy generating industry.

Herein the research on pDCPD-based materials conducted in roughly the last two decades in academia is summarized. Emphasis is laid on ruthenium based initiating systems.

2. Contemporary research directions

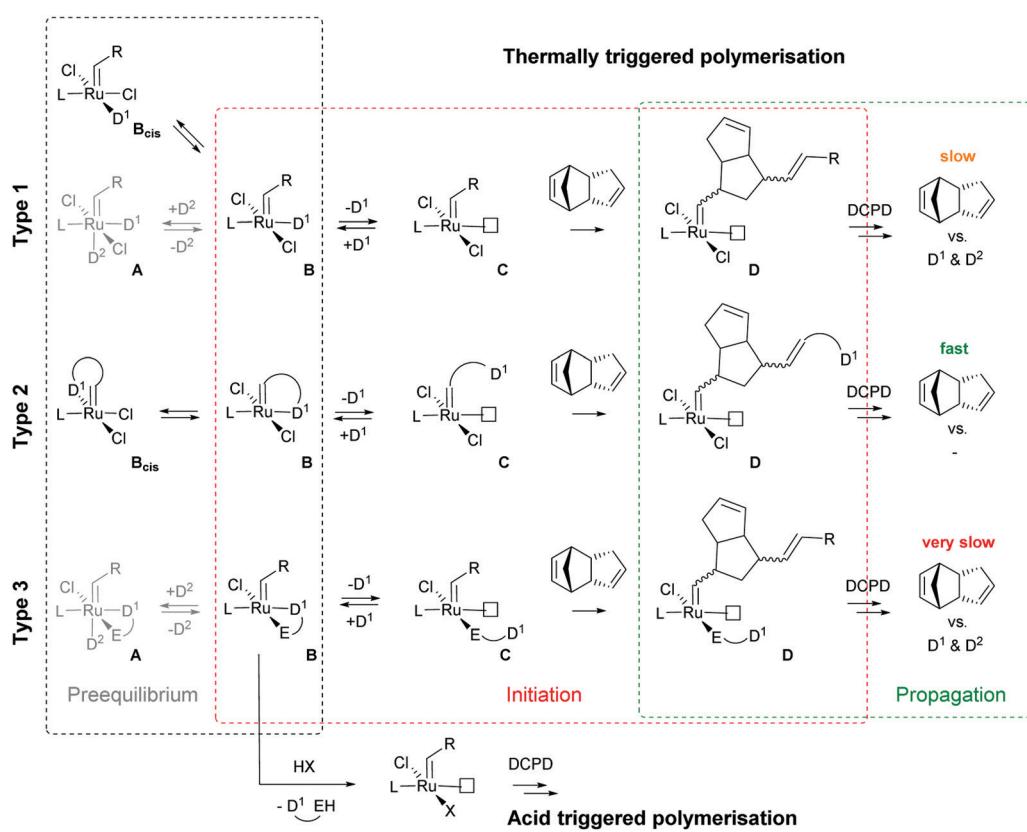
2.1. Processing of DCPD – the need for latent initiators

The initially implemented RIM processing of DCPD is based on mixing two monomer streams, one containing a pre-initiator and the second an activator, just before the combined resin is injected into the mould. Additionally, a retarder is added to adjust the (usually short) induction period, facilitating the

filling of the mould.¹¹ This implementation is by far not ideal when more time to fill the mould (big parts, parts exhibiting shapes with different aspect ratios, and fabrication of reinforced parts) is needed. Furthermore, classical initiation systems are sensitive to moisture and air, limiting also the use of many co-monomers and/or fillers.

Therefore, a lot of attention has been devoted to the development of latent and insensitive initiation systems.¹² Of particular interest is to enable so-called one-component systems. In such resins, the monomers and the initiator are already combined and polymerisation is then started after a predetermined time or by an external stimulus, in most cases elevated temperature. Such one-component resins facilitate RTM and VTRTM but also RIM processes in terms of providing long working time and better chemical compatibility with other ingredients as well as oxygen and moisture. Additionally, less sophisticated process machineries can be employed. Amongst thermally switchable initiators, also initiators which can be triggered by light, acids, redox-reactions and mechanical force have been investigated.^{12–15} Most initiator systems are based on ruthenium because of its high functional group tolerance and insensitivity towards oxygen and protic groups.

2.1.1. Thermally switchable initiators. There are three principal ways to design (well-defined ruthenium based) thermally switchable initiators (Scheme 1). Type 1 systems rely on strong Ru–D¹ bonds (Type 1, **B**). In simplified words, the ligand



Scheme 1 Most common avenues towards latent Ru-based initiators. L is typically a phosphine or an N-heterocyclic olefin; D¹ and D² are typically σ - or π -donor ligands such as amines, phosphines or N-heterocyclic carbenes; E is typically O or S; and R is typically an organic rest like a phenyl group.



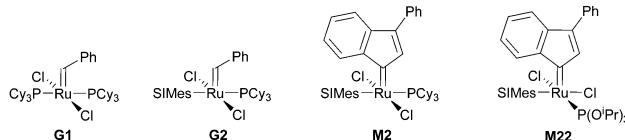


Fig. 1 Commercial Type 1 initiators used for the polymerisation of DCPD. PCy₃ = tricyclohexylphosphine; SIMes = 1,3-dimesitylimidazolin-2-ylidene.

D¹ has to leave the coordination sphere in order to provide an empty coordination site (Type 1, C) for the proper coordination of the monomer.¹⁶

Subsequently the metathesis event takes place providing the initiation (Type 1, D). During propagation, the decoordinated ligand D¹ is competing with DCPD for the vacant coordination site. Therefore, propagation is relatively slow. Upon adding more donor ligand (D²; D² could be the same as D¹), both initiation and propagation are further decelerated.^{17,18} In most publications the commercially available initiators G1^{19,20} or G2^{21,22} are used (Fig. 1) and, if necessary, the working time is adjusted upon addition of additional donor ligands like with amines,¹⁸ phosphines,^{23–25} N-heterocyclic carbenes^{26,27} or phosphite esters.²⁸ Additionally, M2, an analogue of G2, is commercially available and exhibits a better latent behaviour than *e.g.* G2.²⁹ Another way to create initiators that are distinctly more latent is to employ Type 1 pre-initiators exhibiting a *cis*-dichloro stereochemistry (B_{cis}). However, only a few *cis*-dichloro configured initiators of Type 1 are known.³⁰ In this case, the metathetically inactive B_{cis} has to isomerize to the corresponding *trans*-dichloro form before initiation can start. As the only representative of this family, initiator M22 was benchmarked against G2 and M2 and showed by far the highest latency.²⁹ Note that 10–30 ppm initiator (G2, M2 or M22) is sufficient to obtain pDCPD parts with similar mechanical characteristics to industrially manufactured samples.

In a second layout, the Type 2 system, a chelating carbene ligand is used (B). In that case, the decoordination of D¹ is entropically disfavoured and, accordingly, initiation is slowed down. The effect becomes even bigger if the corresponding *cis*-dichloro isomer (B_{cis}) is used. Once initiated (Type 2, D), the chelate effect is cancelled because D¹ is moved away from the metal centre and propagation is relatively fast. Note that addition of donor ligands (used to increase the processing window in Type 1 initiators) could have counterproductive effects because dechelation is accelerated in this case.³¹ As in the case of Type 1 initiators many potential latent compounds have been disclosed,³² but only a few have been described according to their performance in polymerising DCPD.^{33–38} Fig. 2 shows exemplary Type 2 initiators which were tested. Most of them feature a nitrogen as the second ligand atom of the chelate ring (1–3),

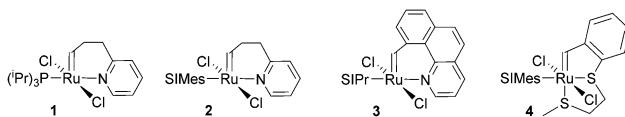


Fig. 2 Selected examples of Type 2 initiators tested in the polymerisation of DCPD.

but also the sulphur-based variant 4 has been described.³⁹ Although the different testing conditions used in the literature do not allow for identifying the best candidates, it is revealed that often subtle changes of the initiator structures cause big differences in their latency. Perhaps this is the reason why such Type 2 initiators are rarely applied in preparing pDCPD in the open research literature, although some of them are even commercialized.^{40–42}

In a third layout, the donor ligand is tethered to an anionic ligand (Type 3, B).^{43,44} Variants featuring two such chelating ligands are also known.^{45,46} Similarly to Type 2 initiators, the chelate effect slows down the initiation, but also propagation is distinctly decelerated. Therefore, this layout is rather used in acid switchable systems (*vide infra*). Finally, a combination of Type 2 and 3, *i.e.* chelation takes place *via* the alkylidene and an anionic ligand, is known.^{47–49}

In the area of potentially less toxic molybdenum and tungsten imido alkylidene complexes, the first latent and considerably air and moisture tolerant initiators for DCPD have been described recently.^{50,51} For more sensitive initiators a protection strategy by encapsulation in paraffin is available.⁵²

As already emphasised, a meaningful comparison of the performance of the different initiators is hard to make. A standardized test protocol, as available for other olefin metathesis reactions, is missing.⁵³ As a first step to establish such a protocol, it is suggested to study the curing of DCPD at low initiator loadings (*e.g.* 30 ppm with respect to DCPD) using thermogravimetric analysis coupled with differential scanning calorimetry (*e.g.* with a heating ramp of 3 °C).²⁹ Additionally the quest towards latent initiators which are soluble in the monomer is underdeveloped. Solvents are undesirable in many processing technologies for DCPD and the solubility of many initiators in DCPD is limited.

2.1.2. Acid switchable initiators. Initiators that are inactive at ambient temperature but can be activated upon addition of another chemical resemble the classical way of processing DCPD in RIM. However, in the case where ruthenium pre-initiators are used, the advantage of a higher functional group tolerance compared to the classical initiator systems is gained. In ruthenium chemistry, the activator for the pre-initiator is an acid, which is able to remove (at least one donor of) the chelating ligand from the central atom (Scheme 1) and is able to provide the anionic ligand, necessary to guarantee the ROMP-activity of the initiator. Amongst processing DCPD *via* the classical methods, also a switchable polymerisation of emulsions by this approach has been described.⁵⁴

2.1.3. Light switchable initiators. In applications like coatings or additive manufacturing light curing resins are desirable. Not surprisingly, research on light triggered olefin metathesis reactions has been conducted over the years.⁵⁵ Nevertheless, research on light curing resins based on ROMP-able monomers in general and on DCPD based resins in particular is scarce. Early work used ill-defined ruthenium–arene complexes and solvated Ru(II) species.^{56,57} This concept was further elaborated leading to several pre-initiators which can be activated with UV-light of 254 nm (and 308 nm) being the key-component for

DCPD based negative resists.^{58,59} A similar concept uses the photo-generation of an N-heterocyclic carbene which subsequently creates an ill-defined initiator.^{60,61} Also Type 1 (e.g. **M22**) and Type 2 thermally latent initiators can be activated by light and polymerize DCPD.^{62,63} Recently, a phosphite ester bearing a Type 1 complex with improved absorbance was disclosed. A formulation containing DCPD and 200 ppm of this compound serving as a photoinitiator was used for stereolithography. Layers were successfully cured for 30–60 s with a light source emitting at 385 nm.⁶⁴ Another recent approach comprises the combination of a Type 1 initiator with a photoredox active pyrylium salt, which allows pDCPD patterning, and photolithography by visible light.⁶⁵ Note that the combination of pyrylium salts and vinyl ethers allows for the metal free, light triggered polymerisation of DCPD, albeit with only low efficacy and without crosslinking.⁶⁶ Finally, the combination of Type 3 initiators with photoacid generators is used for light curing of cyclic olefins, but DCPD was not tested with such initiator systems.^{67,68}

2.2. Influencing the properties of pDCPD

2.2.1. Principles and properties. ROMP of DCPD is a chain growth polymerisation process in which the tricyclic monomer is converted into pDCPD *via* a metal-mediated carbon–carbon double bond exchange process. This implies that the double bonds present in DCPD are still present in the polymer. The polymerisation is driven by the release of strain stored in DCPD and balanced by entropic penalties.⁶⁹ Due to the high ring strain stored in the norbornene part of DCPD, which is approx. 27 kJ mol⁻¹,⁷⁰ the polymerisation is highly exothermic. As revealed by several investigations of the cure kinetics of the reaction with mainly **G1** and **G2**, a polymerisation enthalpy on the order of 300–450 J g⁻¹ (depending on different reports) was measured.^{21,24,71} Liquid DCPD has a density of about 0.97 and is converted into pDCPD with a density of roughly 1.03, which constitutes a volumetric shrinkage of *ca.* 6%.

DCPD can exist in two stereoisomers, the *endo*- and the *exo*-isomer. Typically commercially available DCPD consists of >95% *endo*-DCPD and most studies and applications use *endo*-DCPD. However, *exo*-DCPD polymerises distinctly faster than *endo*-DCPD. The different polymerisation rates were ascribed to steric effects. In *endo*-DCPD the penultimate repeating unit is believed to interact with incoming DCPD, thus slowing down the polymerisation.⁷² However, we hypothesise that the higher steric crowding of the more reactive double bond in *endo*-DCPD (Fig. 3) impedes productive collisions with the metal centre necessary for coordinating the monomer. Proper coordination of the

substrate to the metal alkylidene is known to be the first step in olefin metathesis and should therefore be more facile in the case of *exo*-DCPD.

Polymerising pDCPD produces in many cases and under most conditions a cross-linked, insoluble material. There has been much debate about the chemical nature of the crosslinks in many studies discussed in this article. Three cross-linking reactions are feasible (especially for initiators like **G1** and **G2**). The most obvious is ring-opening metathesis of the second, less reactive double bond leading to cross-linking of the polymer.⁷³ This mechanism operates already at low temperature. The second possibility is olefin addition, which rather takes place at elevated temperatures.^{74–76,78} A third option is oxidative cross-linking, which happens when pDCPD is aging under air (see below).^{77,78} Increased cross-linking is generally reflected in higher glass transition temperatures,⁷⁹ which usually range from 140 to 165 °C (for cross-linked versions). However, even glass transition temperatures higher than 200 °C were recorded for pDCPD upon repeated heating–cooling cycles²² or prolonged heating.⁷⁸

Cross-linking is a main factor for determining the mechanical properties of the material. Upon changing pDCPD's cross-linking density by copolymerisation of either chain extenders or cross-linkers, the impact of crosslinks on the mechanical properties was investigated.^{21,80,81} Typical mechanical properties of pDCPD comprise a Young's modulus in the range of 1.6–2.0 GPa, tensile stress at yield of about 35–70 MPa and elongation at break from 5–100%.^{21,29,71} Unlike other thermosetting materials such as epoxy resins, pDCPD lacks strong non-covalent interactions and thus cross-linking is only due to covalent bonds. This is the reason for the pronounced ductility of pDCPD compared to epoxy resins (with a similar glass transition temperature). The ductility results in the high toughness and remarkable impact performance of pDCPD.²¹ The ductility is conserved even at a temperature of 77 K.⁸² Digging deeper, these favourable properties are attributed to a facile plastic deformation and nano-scale void formation which accommodates the strain.^{83,84} The merit of the mechanical properties of pDCPD was impressively described in a publication on the ballistic performance of pDCPD in comparison with two epoxy–amine systems with comparable glass transition temperatures. pDCPD showed a 300–400% better penetration resistance in ballistic energy dissipation in a temperature range of –55 to 75 °C.⁸⁵

The choice of the initiator (together with the processing conditions) not only determines the degree of cross-linking but also the microstructure of the polymer-backbone. While **G1** produces rather *trans*-double bonds, a higher *cis*-double bond content is obtained with **G2**. The stereochemistry of the pDCPD backbone is another factor influencing the thermal and mechanical properties of the polymer. A nice showcase paper discussing all these aspects influencing the final properties of, in this case, pDCPD aerogels might be instructive for researchers who wish to become active in this field.⁸⁶ Furthermore, in the context of *cis* and *trans* content, it is worth mentioning that molybdenum and tungsten (but no ruthenium) based initiators are known to provide stereospecific ROMP of DCPD, yielding in

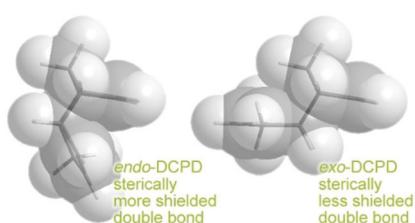


Fig. 3 Space filling cartoons of *endo*- and *exo*-DCPD.



some cases crystalline polymers.^{87–89} Achieving stereospecific ROMP of DCPD with ruthenium based initiators might open the door for materials with better or even new properties.

2.2.2. Durability of pDCPD. The thermal aging of pDCPD is dominated by fast oxygen diffusion limited oxidation affecting the surface to a depth of about 10–100 μm . The oxidised volumes feature a higher cross-linking degree, a higher glass transition temperature, an increased hardness and polarity of the surface and reduced swelling. Addition of stabilisers such as Tinuvin®171 leads to an even harder surface layer. These surface layers were shown to protect the bulk material underneath from oxidation. Even unstabilised pDCPD is extremely resistant to bulk-oxidation and is in this context far superior to *e.g.* poly(propylene).⁹⁰ The high rate of surface oxidation was ascribed to a low apparent activation energy (of only $\approx 45 \text{ kJ mol}^{-1}$)⁹¹ and to the glassy state of pDCPD. The latter feature causes a low termination rate between initially formed peroxy radicals leading to the accumulation of high hydroperoxide concentrations of about 1–2 mol L^{-1} at 50 °C after about 8 h.⁹² The follow up products from hydroperoxide decomposition are then carboxylic acids, aldehydes, ketones and alcohols as well as newly formed C–C bonds. Oxygen incorporation at the surface amounts to approx. 0.5 equiv. O_2 per repeat unit.^{93,94} The aging of pDCPD under high temperature and high pressure in seawater was investigated. The results reveal that for aging at temperatures below the glass transition only oxidative degradation occurs, whereas for aging at higher temperatures a secondary polymerisation process of the material is observed. The water absorption of pDCPD was determined to be 1% (the water diffusion is $8 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ at 25 °C) and the mechanical properties are not compromised by water uptake.⁷⁸

2.2.3. Copolymers of pDCPD. Most copolymerisation reactions performed either use cross-linking ROMP-able or chain extending ROMP-able monomers with the aim to tailor the rheological, mechanical and thermal properties of the resulting thermoset. The respective studies are not discussed here but are mentioned where appropriate within the other chapters of this review. Some effort was made to use biobased cross-linking norbornene derivatives as co-monomers and studies on functionalised isosorbide⁹⁵ and castor-oil^{96,97} have been disclosed.

Chain transfer agents are barely used in (materials directed) pDCPD chemistry because they impede the formation of the cross-linked structure or at least decrease the glass transition temperature of the thermoset. Two studies with monoterpenes demonstrate the principle. One publication reported the synthesis of hyperbranched (soluble) pDCPD upon using β -pinene, limonene oxide or *d*-limonene.⁹⁸ Using less monoterpene the degree of crosslinking of pDCPD was altered and the thermoset was plasticised to a desired degree.⁹⁹ Very low amounts of fluorescent chain transfer agents (not altering the thermal and mechanical properties) were used to study the polymerisation of pDCPD by operando fluorescence microscopy imaging. It was found that the morphology of the precipitated polymers at an early stage persists in the bulk polymer. Strand aggregation was found to be slow and irreversible relative to precipitation.¹⁰⁰

Another type of copolymerisation makes use of the olefin addition occurring at elevated temperature. Substituted cyclopentadiene¹⁰¹ derivatives and substituted maleimide derivatives were employed.^{102,103} Rigid cross-linking monomers enhanced the thermal and dynamic mechanical properties.

Thermoset blends of pDCPD and epoxy resins resulted in macroscopically phase separated systems featuring two glass transition temperatures. In the blend the higher strength of the epoxy resin can be greatly retained while the fracture toughness was increased.^{104,105} The blends were used for gluing carbon fibre reinforced composites with steel. The epoxy-pDCPD blend adhesives realized much higher bond strengths compared to either neat epoxy or neat pDCPD, which was attributed to an increased shear toughness of the blend.¹⁰⁶ Similarly, the blend of polyethylene wax and pDCPD was studied; here thermally induced cross-linking between pDCPD and the wax was postulated.¹⁰⁷

2.2.4. Nanocomposites of pDCPD. The improvement of the physical properties of pDCPD takes centre stage in this research. First, it is aimed at enhancing ideally both the strength and toughness of pDCPD. Second, the physical properties of pDCPD are changed according to the needs of specialised applications.

Copolymerisation of polyhedral oligomeric silsesquioxanes with DCPD did not result in significant property changes of the composite material.¹⁰⁸ However, the use of vinyl-functionalised silica particles (diameter 0.3–0.7 μm) led to a distinct enhancement of the toughness of the materials. Upon just adding 0.2 wt% of the particles the tensile toughness increased by a factor of 14, while the yield strengths decreased by about 10% compared to pDCPD without particles.¹⁰⁹ In follow-up work, the silica particles have been differently functionalised and the effect of functionalisation on the mechanical properties of pDCPD composite materials was studied. Ethyl-functionalised particles were found to increase the strength and toughness.^{110–112} Poly(styrene) coated silica nanoparticles were shown to decrease the friction coefficient and the wear rate of pDCPD.^{113,114} An older study reports norbornene-capped silica particles and an improved wear resistance of the PDCPD/silica nanocomposite processed by RIM.¹¹⁵ Also MoS_2 pDCPD nanocomposites were investigated for their wear resistance.¹¹⁶ The outstanding dielectric characteristics of pDCPD (which are similar to those of poly(propene)) motivated development of a RIM process allowing further improvement of them. By incorporation of 10% fumed silica, a permittivity of 2.8 was obtained and the mechanical properties were not compromised significantly.¹¹⁷ Another example aiming in the same direction comprised the use of BaTiO_3 nanoparticles (5 wt%) for increasing the permittivity of pDCPD (1.7) to 2.4 whereby the breakdown strength was only reduced by 13%.¹¹⁸ Work on montmorillonite nanocomposites was performed.^{119–122} Most interesting is a contribution in which so-called intergallery-surface-initiated ROMP was used to obtain an exfoliated montmorillonite nanocomposite with 50% increased stiffness in compression.¹²³

The most influential work on pDCPD nanocomposites was published in 2008. Norbornene functionalised multiwalled carbon nanotubes were used in low loadings (<0.5 wt%) and the resulting nanocomposites exhibited a slightly enhanced Young's modulus of 2.09–2.14 GPa (neat pDCPD 2.07 GPa) but a



distinctly enhanced strain at break up to 51.8% (neat pDCPD 5.75%) resulting in a toughness of about 25 MPa (2.44 for the reference).¹²⁴ A different carbon nanotube functionalisation route was disclosed and the derived material tested with DCPD.^{125,126} Non co-polymerisable carbon materials used as nanofillers comprise expanded graphite nanosheets,¹²⁷ vapour grown carbon fibers and graphene oxide.^{128,129}

2.2.5. Fibre reinforced pDCPD. Today's composites consist mainly of glass or carbon fibres (mats) embedded into a thermoset matrix based on epoxy- and polyester chemistry. Resin transfer moulding and vacuum infusion are the most frequently used processing methods. pDCPD is an interesting alternative to these conventional matrices, for two main reasons. First, the viscosity of a typical DCPD based resin (≈ 10 cPs) is similar to that of water and much lower than that of conventional resins. Thus, infiltration of the fibre mats, especially when big parts are manufactured, is less energy and time consuming. Second, pDCPD is less brittle than many other matrices of similar strengths, resulting in an appealing impact resistance.¹³⁰ A pDCPD based glass fibre composite and an equivalent epoxy composite were compared and revealed a greatly superior damage resistance of the pDCPD based parts.¹³¹ Since interfacial adhesion between the fibres and the matrix is an important factor for the properties of the composites, different glass-fibres were tested.¹³² Silanisation of the glass fibre surface has beneficial effects on interfacial adhesion.^{133,134} Degradation tests of pDCPD glass fibre composites *versus* epoxy based systems under hydrothermal conditions revealed the superiority of the pDCPD system. The results were rationalised by the lower water uptake of the pDCPD based parts.^{135,136} Thermal aging of glass fibre composites under air caused oxidation of the surface region (~ 100 μm). Aging at 150 $^{\circ}\text{C}$ induced significant degradation of the fibre-matrix interface, while aging at 100 $^{\circ}\text{C}$ for 6 months had little effect on the fibre-pDCPD interface properties.¹³⁷ Polyethylene fibre¹³⁸ and carbon fibre reinforcement of pDCPD were also investigated.^{139,140}

Another type of filling is aimed at reducing the cost of pDCPD and its use in structural applications. Wollastonite, a cheap filler with a needle-like crystal shape and high thermal stability, was used to prepare composite materials with pDCPD. Up to 67 wt% of the CaSiO_3 mineral was incorporated by planetary mixing and the composites' high compressive strength of more than 100 MPa revealed them to be superior to high strength concrete (63 MPa).¹⁴¹ Recently, DCPD-based resins were tested for their ability to penetrate into rocks and to reinforce the rock's mechanical strength. Due to the low viscosity of the resin, the desired diffusion was obtained in dry and 50% water saturated rocks. Upon curing the storage modulus and the flexural strengths were improved, qualifying the resin for down-hole applications such as sealants or plugs.¹⁴²

2.2.6. DCPD as 'glue' in self-healing materials. In service, composite parts are subjected to diverse forces, which cause, besides visible and easily detectable failures, hardly visible or even invisible micro-cracks in the polymer matrix. Therefore, a reduction in fibre-dominated properties such as the tensile strength and other material fatigue occur.¹⁴³ If these micro-cracks

coalesce in structural composites, delamination and fibre fracture follow. As a means to mitigate such effects, a self-healing function can be added to the material. Self-healing is a process by which a damaged material can at least partially restore its original properties. One of the most prominent self-healing strategies relies on ROMP of DCPD and similar strained cyclic olefins.¹⁴⁴ Healing is accomplished by the stress triggered release of microencapsulated DCPD from a urea-formaldehyde shell¹⁴⁵ and polymerisation with the initiator, which is embedded in the epoxy-based composite matrix. Initially **G1** was used as the initiator but since then many efforts were made to improve the thermal stability, the processability and the activity of the initiator.¹⁴⁶⁻¹⁴⁹ Thermal stability is of central interest. During curing of the matrix material, the initiator is usually exposed to high temperatures for prolonged times as well as to potential initiator poison (e.g. oxiranes and amines in the case of epoxy-resins). One approach is to encapsulate the initiator (**G1**) in wax,^{150,151} or to use thermally and chemically more stable variants.¹⁵²⁻¹⁵⁶ Another research direction discloses alternative healing agent carriers such as hollow tubes and fibres,^{143,144} or microvascular networks.¹⁵⁷ A typical application of self-healing comprises wind turbine blade materials. This is one of the examples in which the idea of self-healing is reasonable, because wind turbine blades face high risks of damage causing high repair costs.^{158,159}

2.3. Emerging processing of pDCPD

2.3.1. Frontal polymerisation. In frontal polymerisation, a monomer is converted into its polymer directionally in a localized reaction zone. In thermal frontal polymerisation, the polymerisation is started by employing heat and then the polymerisation enthalpy sustains further polymerisation. This leads to transmigration of the polymerisation zone through the volume of the monomer. As a prerequisite, the formulation must have a low rate of polymerisation at the initial temperature but have a very high polymerisation rate at and below the adiabatic polymerisation temperature (which is a technical term for the temperature reached if the polymerisation went to completion without heat loss). The application of frontal polymerisation in the fabrication of fibre-reinforced polymer composite materials is of particularly high interest because of its high energy saving potential. In the light of success in fibre-reinforced pDCPD composite materials, DCPD-based frontal polymerisable resins are researched.

In 2001, the first report of frontal Ring-opening Metathesis Polymerisation was published. In this early report, high purity DCPD, **G1** and triphenylphosphine as a retarder were introduced. The formulation was prepared above the melting point of DCPD and was then quickly cooled to 27 $^{\circ}\text{C}$. The actual frontal polymerisation was then performed on solid mixtures. A maximum front temperature of about 205 $^{\circ}\text{C}$ propagating with a front velocity of 2.6 cm min^{-1} was obtained when the formulation contained 2000 equiv. of DCPD, 1 equiv. of **G1** and 2.6 equiv. of triphenylphosphine.²³ In follow-up work, **G2** in combination with 4-dimethylaminopyridine as the retarder was introduced as the initiating system. Maximum front



temperatures of around 200 °C were found when the formulation contained 16 000 equiv. of DCPD, 1 equiv. of **G2** and between 1 and 8 equiv. of 4-dimethylaminopyridine. The variation of the retarder's concentration led to different front velocities, which were between 7.5 and 2.2 cm min⁻¹. The pot life of the liquid formulation (toluene was used to keep DCPD liquid) was improved to about 20–30 min.¹⁶⁰ As an alternative to 4-dimethylaminopyridine, limonene was tested as a retarding agent. Limonene is a chain transfer agent and thus, albeit frontal polymerisation was feasible, the desired mechanical properties of pDCPD were lost.¹⁶¹ Highly reactive *exo*-DCPD has been tested as a monomer in frontal polymerisation with **G2** decelerated by 4-dimethylaminopyridine. Low **G2** loadings of 10 ppm were sufficient to provide frontal polymerisation in this case. However, the pot life of these formulations was still about 20 min.¹⁶² The pot life issue was tackled by using aliphatic phosphite ester derivatives as retarders for **G2**. By varying the phosphite ester structure and concentration, a pot life of (*endo*)-DCPD-based formulations between 0.25 and 30 h was obtained while still allowing the frontal polymerisation to proceed. The velocity can be adjusted between 1 and 8 cm min⁻¹ (Fig. 4).²⁸ Such a high pot life is the key for industrial applicability and the same group demonstrated the rapid fabrication of parts with microscale features and carbon-fibre-reinforced polymer composites. The mechanical properties of such processed parts are similar to those of pDCPD cured under conventional conditions. Accordingly, frontal polymerisation processing allows for reducing energy requirements and cure times. Especially for the processing of fibre-reinforced polymer composites a huge saving of time and energy is achieved when compared to conventional epoxy-based parts. Furthermore, three-dimensional printed structures can be fabricated with these formulations. Upon tuning the retarder concentration, free-standing elastomeric gels containing prepolymerised DCPD are obtained. These gels can be extruded from a print head and frontally polymerised upon applying heat to the substrate. In such a process, simultaneous free-form printing of thermosets is achieved.¹⁶³ Numerical studies of the initiation and propagation of the polymerisation front in fibre-reinforced composites were conducted to better understand frontal polymerisation of DCPD.¹⁶⁴ Lately, the frontal copolymerisation of DCPD with other norbornene derivatives was disclosed with the aim to tune the material properties and simultaneously improve the efficiency in FROMP-based material manufacturing. In doing so, an unexpected increase in the front

velocity when copolymerising DCPD with dinorbornenyl cross-linking monomers was found and rationalized.¹⁶⁵

2.3.2. Additive manufacturing of pDCPD. Possibilities for additive manufacturing comprise the already mentioned stereolithographic process⁶⁴ and frontal polymerisation based direct ink-writing.¹⁶³ The latter was further improved towards 3D printing of thermally insulated pDCPD. The effect of the extrusion pressure and operating temperature on the thermal properties and the surface morphology of the printed pDCPD was studied and a thermal conductivity of 0.1 W m⁻¹ K⁻¹ was obtained under optimised conditions.¹⁶⁶

2.3.3. Miscellaneous processing of pDCPD. Electrospinning was used to produce sub-micrometre thick fibres of pDCPD. The spinning solution was composed of DCPD, dichloromethane and **G2**. An aged solution exhibiting the proper viscosity was then used for electrospinning. Electrospinning was only possible in a limited time frame due to the rapidly changing viscosity of the solution. However, these fibres collected exhibited Young's moduli larger than the typical values for bulk pDCPD.¹⁶⁷

Another processing method is surface-initiated ROMP from the vapour phase. The first report used, amongst other monomers, DCPD from the vapour phase for patterned growth of pDCPD on surfaces with microcontact printed and physisorbed **G2**.¹⁶⁸ Later, surface initiated ROMP of *exo*- and *endo*-DCPD was studied using initiators covalently attached to gold and silicon substrates. Approx. 400 nm thick pDCPD films were obtained in less than 1 min of polymerisation and no significant differences in thickness were observed for the different stereoisomers. Film thicknesses ranging from tens of nanometres to hundreds of nanometres could be achieved upon adding decane as an unreactive diluent to the vapour phase. The films provide effective barriers to the diffusion of aqueous ions in excess of $1 \times 10^6 \Omega \text{ cm}^2$ and exhibit a reduced Young's modulus of 15 GPa.⁷⁰

Finally, the polymerisation of DCPD in a microemulsion leading to stable pDCPD latexes which can be further processed should be noted. Water soluble, acid switchable initiators were used to polymerise DCPD (and DCPD/cyclooctene mixtures) in an Emulgin® B3 stabilised microemulsion. With low initiator loadings of about 200 ppm, almost complete polymerisation was found and stable latexes with particle diameters ranging from 255 nm to 315 nm and low coagulate content were obtained.⁵⁴ Prior work disclosed carbon nanotube loaded latexes.¹⁶⁹ Another emulsion based approach is the preparation of particles featuring interfacially assembled nanoparticle-conjugated lipase. Such 10 µm big functional particles in which pDCPD serves as the glue displayed an increase in catalytic efficiency of the lipase when compared to the native enzyme. The particles could be magnetically recovered, thanks to the magnetic nanoparticles used. Moreover, the immobilized lipase exhibited enhanced thermal and pH stability^{170,171} and could be operated in deep eutectic solvents.¹⁷²

2.4. Porous pDCPD

2.4.1. Macroporous pDCPD by chemically induced phase separation. Chemically induced phase separation (also named chemical cooling, polymerisation-induced phase separation or

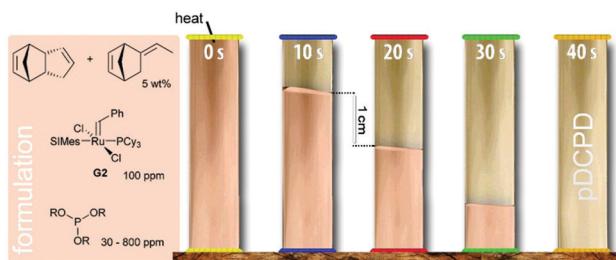


Fig. 4 Frontal polymerisation of pDCPD according to ref. 28.



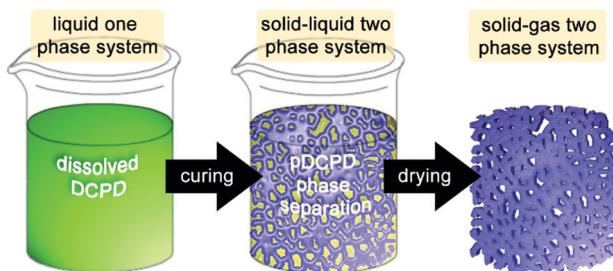


Fig. 5 Cartoon of the process chemically induced phase separation for the preparation of macroporous pDCPD.

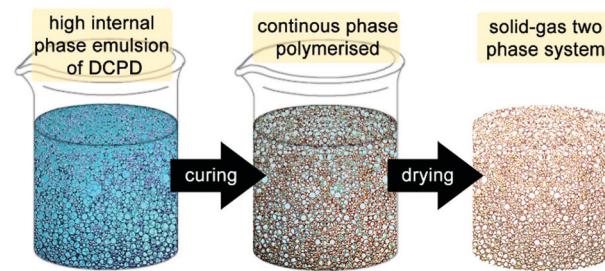


Fig. 6 Cartoon of the high internal phase emulsion templating route to prepare open porous macroporous foams.

reaction-induced phase separation) is a method to produce macroporous thermosets used *e.g.* in separation applications. Essentially, this methodology is based on polymerising a monomer dissolved in a solvent which is a bad solvent for the created polymer. The initially homogeneous solution phase-separates upon polymerisation and eventually the solvent is removed, generating a macroporous structure (Fig. 5).

For DCPD, 2-propanol is a suitable solvent for this purpose and allows for preparing closed or open cell porous monoliths depending of the 2-propanol share. Above 30 wt% of 2-propanol content, the porous structure consists of agglomerated spherical pDCPD particles (of about 3–4 μm). Porosities of up to 80% were obtained¹⁷³ and monoliths exhibiting a gradient porosity were accessible.¹⁷⁴ Additionally adding norbornene-functionalized poly(ethylene glycol) oligomers allowed for a decrease in the pore size and a related increase in the internal surface area.¹⁷⁵

However, for many applications, the modification of the surface is desirable, if not necessary. The surface grafting of initiators for atom transfer radical polymerisation has been demonstrated and used to graft dense poly(methylmethacrylate) onto pDCPD. The process comprises three steps, with the thiol–ene reaction of mercaptoethanol with the double bonds of pDCPD being the key step.¹⁷⁶ Furthermore, the double bonds can be brominated (forming a 100–200 nm thick brominated layer) and it has been demonstrated that subsequent nucleophilic substitution with amines yields monolayers on pDCPD.¹⁷⁷ Epoxidation with *m*-chloroperoxybenzoic acid generates an approx. 10 nm thick layer of oxiranes. Subsequent ring opening with amines provides the installation of the desired functionality in a second step.¹⁷⁸

2.4.2. Macroporous pDCPD by emulsion templating. An alternative way to prepare macroporous polymers is high internal phase templating. In this case the liquid monomer used as the minority phase should be immiscible in another liquid (the majority component, typically 80–99 vol% is used) and upon addition of a suitable surfactant and agitation a high internal phase emulsion forms. In such an ideally kinetically stable situation, the majority phase forms droplets within the continuous phase made up by the monomer. Then the initiator is added and the emulsion is cured in a mould. After solidification of the continuous phase, the majority phase is removed, typically resulting in fully opened polymer foams containing spherical voids (of several μm in diameter) interconnected by windows (Fig. 6).¹⁷⁹

The first attempt to template DCPD failed, presumably due to an insufficient emulsion stability at the elevated temperature needed for curing.¹⁸⁰ However, using water as the majority phase, Pluronics L-121 as the surfactant and M2 as the initiator enables the preparation of high internal phase templated DCPD of about 80% porosity and exceptional mechanical properties compared to other high internal phase templated polymers.¹⁸¹ However, it was realized that the pDCPD monoliths quickly and fully oxidise at elevated temperature under ambient conditions yielding a polymer with an empiric sum formula of $\text{C}_{5.2}\text{H}_{6.4}\text{O}_{1.9}$. The oxidation goes in hand with a stiffening of the foam. Nevertheless, the liability of oxidation constitutes the material's Achilles heel in many potential applications. Upon varying the DCPD to water ratio from 50 : 50 to 20 : 80 open porous monolithic polymers of different porosities could be prepared, whereby the openness of the foams of low porosity is a peculiarity within high internal phase templated polymers.¹⁸² The feature sizes of the foam, *i.e.* void and window sizes, can be determined upon variation of the surfactant amount (10–0.25 vol% with respect to DCPD). Void sizes between 3 and 70 μm can be obtained. Thereby it was revealed that the mechanical properties of the foams are distinctly dependent on the surfactant amount used. Especially when reducing the surfactant amount below generally accepted values in the field, ductile open porous polymer foams with 80% porosity and Young's moduli of about 110 MPa were prepared.¹⁸³ A comprehensive investigation of the mechanical properties of unoxidised pDCPD foams of 90–50% porosity using tensile testing revealed Young's moduli between 31 and 416 MPa and moduli of toughness between 600 kJ m^{-3} and 2 MJ m^{-3} .¹⁸⁴ Similarly, membranes are easily accessible by doctor blading. Open-cellular macroporous membranes with about 80% porosity and 180 μm thickness are characterized by a Young's modulus of about 125 MPa and an ultimate strength of 3.1 MPa at an elongation of about 20%.¹⁸⁵

Similar membranes obtained from copolymerizing norbornene and DCPD were used as separators in lithium-ion batteries. A comparison with cells made from conventional poly(ethylene)-based separators revealed their applicability despite the presence of unsaturation in the polymer backbone. The combination of the high porosity and good wettability of the separators suggests that such considerably thick separators might be useful in bigger lithium-ion batteries with increased safety issues.¹⁸⁶ Like in the case of the separators, copolymerisation of



other ROMP-able monomers has been studied and its effects on the mechanical properties^{187,188} and the foam's swelling behaviour have been disclosed.¹⁸⁸

Amongst copolymerisation, the properties of the foams can be influenced upon the addition of inorganic nanoparticles. Magnetic foams were obtained by adding up to 30 wt% $\gamma\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ nanoparticles to the emulsion and subsequent curing. The oxides were mainly found at the surface of the polymeric phase and the good casting quality of the samples was maintained. Burning off the polymeric phase yielded macroporous Fe_2O_3 , demonstrating a way towards high internal phase templated ceramics.¹⁸⁹ Similarly, zinc oxide nanoparticles were used to prepare pDCPD nanocomposite foams. Subsequent calcination yielded macroporous ZnO foams, which showed an appealing catalytic performance in the catalytic wet air oxidation of bisphenol A.¹⁹⁰ Furthermore, $\text{TiO}_2@\text{pDCPD}$ has been described and tested in the photocatalytic degradation of 4-nitrophenol.¹⁹¹ Later, the composite foam's mechanical properties with and without antioxidants have been disclosed.¹⁹² In another study, nanoparticulate metal-organic frameworks (MOFs) were used to obtain 100 μm thick, fully open, hierarchically porous hybrid membranes. Up to 14 wt% of MIL-100(Fe) nanoparticles were incorporated, resulting in an increase of the microporosity from 5 to about 130 $\text{m}^2 \text{ g}^{-1}$. The MIL-100(Fe) $@\text{pDCPD}$ membranes showed an appealing catalytic activity in Friedel-Crafts alkylation in batch and flow-through mode, thereby demonstrating the preserved accessibility of Lewis acidic sites in the MOF.¹⁹³ Another study utilized CuO and $\text{ZnO}@\text{pDCPD}$ foams to grow MOFs (HKUST-1(Cu) and MOF-5(Zn)) upon addition of ligand solutions. In this way, up to about 75 wt% MOF loading of the foams was obtained and micropore accessibility was greatly retained. The hydrolytical instability of the MOFs was distinctly reduced in the MOF $@\text{pDCPD}$ composites. This feature enabled the preservation of the composite's CO_2 sorption capacity under humid conditions for at least 20 cycles.¹⁹⁴ Another example of stabilization within macroporous pDCPD foams comes from encapsulating enzymes. Lipase was incorporated into pDCPD foams upon adding the enzyme to the aqueous phase of the high internal phase emulsion. Curing was done at room temperature and the encapsulated lipase was found to be active under harsh reaction conditions not complying with free lipase. Further, the lipase $@\text{pDCPD}$ retains over 50% activity after 10 cycles of reuse.¹⁹⁵ The above mentioned high internal phase emulsion approach was initiated to resolve recovery issues of 10 μm big pDCPD particles with interfacially assembled nanoparticle-conjugated lipase mentioned above.¹⁷⁰

Post-polymerisation functionalization of emulsion templated pDCPD in the unoxidised state was performed with epoxidation,¹⁹⁶ bromination,¹⁸⁵ thiol-ene¹⁸¹ and inverse electron demand Diels-Alder reactions. In the latter approach, tetrazines (e.g. 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine) were reacted with the double bonds of pDCPD foams resulting in functionalisation of up to every second repeating unit with a potential metal chelating ligand.¹⁹⁷ The same reaction was also used with linear pDCPD and the gelation of the resulting polymer with

metal ions was studied.¹⁹⁸ Epoxidation of pDCPD monoliths was performed in supercritical CO_2 . In that respect, it was revealed that the foams exhibit an unusually high uptake of sc CO_2 at zero swelling. The sc CO_2 treatment creates additional mesoporosity within the foam walls and a sequence of epoxidation followed by aminolysis with ethylenediamine yielded 11.4 mmol g^{-1} of nitrogen incorporated into the foam walls.¹⁹⁶

As already mentioned, pristine pDCPD foams react with elemental oxygen from air yielding (amongst other functional groups) stable hydroperoxide moieties within the polymer scaffold. The hydroperoxide-containing pDCPD foams were then used to oxidise and sequester Demeton-S and 2-chloroethyl ethyl sulphide, employed as models for chemical warfare agents. The simplicity of the detoxification is believed to hold high promise for the development of self-decontaminating filter media.^{199,200} Another exploitation of the porous material's high tendency to oxidize was its use as an oxygen scavenger material. However, in this application emulsion templated poly(norbornadiene) proved superior to emulsion templated pDCPD.²⁰¹ Oxidation in air leads to a stiffening of the macroporous monolithic specimens to such a degree that their cellular structure is not lost upon heating (up to 1400 $^{\circ}\text{C}$) under an inert atmosphere. Thus, the 'fixation' upon oxidation allowed for the preparation of monolithic open macroporous carbons of 80–85% porosity featuring void diameters in the range of 87 to 2.5 μm . The porous carbon materials were characterized by carbon contents higher than 97%, electronic conductivities of up to 2800 S m^{-1} , Young's moduli of up to 2.1 GPa and specific surface areas of up to 1200 $\text{m}^2 \text{ g}^{-1}$. All these values were mainly depending on the carbonisation conditions.²⁰²

2.4.3. Aero- and xerogels made of pDCPD. Aerogels are typically obtained by supercritical drying of wet polymer gels and generally feature extremely low density, high surface areas and attractive dielectric, thermal and acoustic properties. Upon supercritical drying shrinking occurs and aerogels lose about 10% of their initial volume (Fig. 7).

Alternatively, ambient pressure drying processes are employed. In this case the volume shrinkage is much bigger (typically 50%) and pore structure damage occurs. High capillary forces are responsible for this phenomenon. The first pDCPD based aerogels were published in 2007 and were obtained by polymerizing a solution of DCPD with G1 targeting an aerogel density of 0.06 g cm^{-3} . The system was further investigated by varying the target density, the initiator loading, the solvent

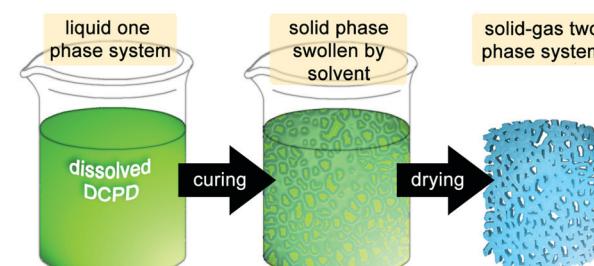


Fig. 7 Schematic preparation of aerogels.



and the drying conditions (supercritical CO_2 drying *vs.* conventional drying). Typical pDCPD aerogels obtained within this study were characterized by a density of 0.06 g cm^{-3} , a pore volume of $0.89 \text{ cm}^3 \text{ g}^{-1}$, an average pore diameter of 15 nm , a surface area of $235 \text{ m}^2 \text{ g}^{-1}$ and a thermal conductivity of 22.9 mW mK^{-1} . However, the preparation of homogenous and uniform specimens was difficult to achieve.²⁰³ Key to improving this issue is precise control over the viscosity and gel time and gelation can be manipulated by reducing the amount of cross-linking through co-polymerisation with a non-crosslinking monomer. It was shown that only small additions of norbornene (1–10 wt%) increase the viscosity at the sol–gel transition by several orders of magnitude, resulting in better uniformity of the samples. The finding was applied to the coating of cylindrical and spherical surfaces with pDCPD aerogel films, which is particularly challenging because shear forces can additionally damage the growing gel network.²⁰⁴ This work was further extended towards other non-crosslinking but functionalized monomers (*e.g.* Fig. 8, $\text{R} = \text{CH}_2\text{I}$) and the effect of functionalisation on the morphology of the aerogels was studied.²⁰⁵ Post-polymerisation iodination (and bromination) was tried in a forthcoming study. Because only limited control over the amount and the uniformity of halide incorporation was obtained, the incorporation of iodide (and also tributyltin) groups was preferably accomplished *via* copolymerisation of accordingly substituted norbornene derivatives. Such obtained aerogels were aimed at providing high-Z tracer element substituted organic aerogels for use in inertial confinement fusion.²⁰⁶

Switching from **G1** to **G2** as the initiator caused severe deformation of the wet gels during processing (swelling in toluene) yielding aerogels unsuitable for any application. This issue was resolved by performing free radical polymerisation of methyl methacrylate in the pores of the wet gel and well-defined aerogels could be obtained.²⁰⁷ The phenomenon is explained by a synergism related to the nano-topology of the

two components. It was shown that upon drying the macroscopic deformation of wet gels is accompanied by coalescence of initially formed polymer-nanoparticles that form non-mass-fractal secondary particles. While in the case of neat pDCPD it is believed that these secondary particles further rearrange in such a way that the secondary particles move in the empty space of the others, this movement is impeded in the presence of poly(methyl methacrylate) and thus the structure is better conserved.²⁰⁸ Operando fluorescence microscopy imaging supported the findings.¹⁰⁰ On a molecular level, this behaviour was attributed to the higher *trans*-content of pDCPD polymerised with **G1** when compared to pDCPD made with **G2**. It was concluded that higher *trans*-content makes pDCPD more rigid, while higher *cis*-content results in increased malleability.⁸⁶ Accordingly, the swelling of *cis*-enriched pDCPD (in a nonpolar solvent) should be higher than of *trans*-enriched pDCPD. Indeed, preparing xerogels with the initiator-systems $\text{Na}[\text{W}_2(\mu\text{-Cl})_3\text{Cl}_4(\text{THF})_2](\text{THF})_3/\text{phenylacetylene}$ (**5**) yielded heavily deformed specimens with high *cis*-content. Their swelling in toluene was studied and compared to samples prepared with **G1**. The xerogels prepared with **5** increased their volume by more than a factor of 100, while xerogels obtained from **G1** did not swell at all.²⁰⁹ The swelling behaviour of the **5**-retrieved pDCPD xerogel was further studied using 44 different solvents. From these data, the Hansen solubility parameters and the Flory–Huggins parameter χ_{12} of mostly *cis* pDCPD were derived. The xerogels were particularly useful for separating chloroform from water.^{210,211}

As is the case for all other porous pDCPD variants, also the aerogels are prone to oxidative degradation under ambient conditions. Although the oxidized variants have never been studied, an approach to mitigate this issue was published. Upon hydrogenation with *p*-toluenesulfonyl hydrazide, hydrogenated pDCPD aerogels became accessible. The improved oxidative stability was proven by thermolysis studies at 135°C for 2 h under ambient conditions. While the pDCPD samples turned brownish and shrank and oxidation products were identified, the hydrogenated versions stayed colourless and no typical pDCPD oxidation products were observed in the infrared spectra. However, also the hydrogenated aerogels shrank considerably during the thermal treatment.²¹²

2.4.4. Nanoporous membranes from DCPD only. Solid, dense membranes fabricated from DCPD (5000 equiv.) polymerised by **G1** (1 equiv.) allow for separating molecules with molecular weights of $100\text{--}600 \text{ g mol}^{-1}$ based on the concept of cross-sectional area cut-off (and not based on molecular weight cut-off usually used in organic solvent nanofiltration). It was reasoned that swollen membranes feature polydisperse subnanometer-sized openings between the polymer chains allowing small molecules to diffuse through. Molecules with cross-sectional areas above 0.50 nm^2 permeated with a flux 10^4 to 10^5 times slower than molecules with cross-sectional areas below 0.40 nm^2 .²¹³ This finding was utilized to separate palladium complexes and phosphines used in Buchwald–Hartwig and Sonogashira coupling reactions from the products by simple nanofiltration.²¹⁴ Similarly, the separation of mixtures of fatty acid triisobutylamine salts by such organic solvent

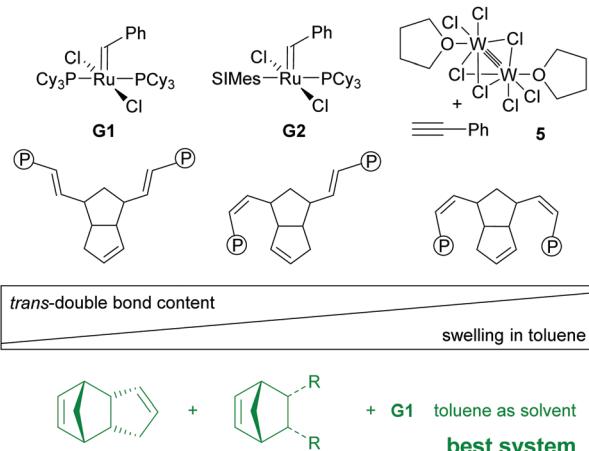


Fig. 8 Initiators used for the preparation of aerogels and the preferred stereochemistry of the double-bond in the repeating unit, being decisive for the aptitude in aerogel synthesis; the best systems are late gelating mixtures of DCPD with less than 10 mol% non-crosslinking monomer ($\text{R} = \text{H}, \text{CH}_2\text{I}, \text{Sn}(\text{iBu})_3$) cured with **G1** in toluene.



nanofiltration membranes was studied. Bigger *cis*-fatty acid salts (oleic, petroselinic, vaccenic, linoleic, and linolenic acid) could be separated from smaller saturated (stearic acid) and *trans*-fatty acid (elaidic acid) salts based on their cross-sectional areas. A pressure-accelerated process for obtaining fluxes sufficient for industrial purification facilities was developed.²¹⁵

2.4.5. Membranes from DCPD and reactive block-copolymers.

Membranes with bigger pores have been prepared by combining polymerisation-induced phase separation and block-copolymer templating. Specifically, a mixture of a norbornene-functionalized poly(styrene)-poly(lactide) diblock copolymer (**6**) and DCPD in tetrahydrofuran was polymerized and the etchable polylactide block was then removed upon treatment with NaOH (Fig. 9). The resulting membranes featured remarkable mechanical properties (Young's modulus close to 1 GPa, ultimate strength of about 30 MPa at an elongation of roughly 10%) and a bicontinuous structure percolating throughout the membrane. The average pore diameter was around 20 nm and the material featured a narrow pore size distribution.^{216,217} Gas and liquid transport measurements through such membranes were performed and revealed their suitability for ultrafiltration. The molecular weight cut-offs can be tuned by changing the size of the constituent blocks in the templating copolymer.²¹⁸ Only polymerising a mixture of the norbornene-functionalized poly(styrene)-poly(lactide) diblock copolymer and DCPD (*i.e.* leaving out the solvent) led to the formation of nanoporous monoliths with aligned cylindrical domains. The alignment was obtained by pressing the blend of unpolymerised (macro)monomers through

a channel before polymerisation occurred. Retardation of the polymerisation was necessary and was accomplished by adding triphenylphosphine to the initiator (**G1**). Upon etching away the poly(lactide)-block, monoliths featuring a specific surface area of about $130 \text{ m}^2 \text{ g}^{-1}$, pore diameters on the order of 10 nm and similarly good mechanical properties to those described for solvent-borne membranes were obtained.²¹⁹ Changing the reactive diblock-copolymer used above for a specially designed triblock-copolymer allowed for the preparation of stimuli responsive porous membranes.²²⁰

2.4.6. Anion exchange membranes.

Research on alkaline anion exchange membranes targets mainly the use in alkaline fuel cells. The reduction of cost and methanol crossover is envisaged. pDCPD based permanently cationic membranes are a particular class of materials in this context. In a first report in 2009 tetraalkylammonium-functionalized norbornene (**7**) was copolymerized with DCPD in chloroform and upon casting and heating the solvent evaporated, yielding thin films. Exchange of the iodine counterion for hydroxide gave the alkaline anion exchange membranes. A composition of 1 part DCPD to 0.5–1 part **7** delivered the best results with respect to mechanical integrity (ultimate strength between 16 and 2 MPa at an elongation of roughly 7–26%) and hydroxyl conductivity ($14\text{--}18 \text{ mS cm}^{-1}$ at 20°C). Dimensional swelling in methanol at 60°C was negligible.²²¹

Similarly to the reactive diblock-copolymer discussed above, macromonomer **8** was used in the copolymerisation with a mixture of DCPD and cyclooctene, yielding membranes that have a bicontinuous morphology. In other words, a hydrophobic network featuring hydrophilic conduction paths was established. The resulting membranes exhibited hydroxide conduction as high as 120 mS cm^{-1} in water at 60°C . However, their mechanical properties were not sufficient for practical applications.²²² This issue was resolved by roughly doubling the molecular mass of the diblock-copolymer. In this case, the conductivity dropped to a still high 98 mS cm^{-1} . Controlled membrane swelling led to about 120% wt% water uptake, whereby the membrane's mechanical integrity prevented excessive water uptake. Qualifications in fuel cells were performed and resulted in increased power and current density compared to a commercial Tokuyama A201 membrane tested under the same conditions.²²³

Divalent bis(terpyridine)ruthenium(II) based monomer **9** and DCPD were used to prepare membranes as outlined in the previous studies. The DCPD to **9** molar ratios employed were 2:1, 5:1 and 10:1. Hydrogen carbonate and hydroxide conductivities (19.6 , 28.6 and 27.0 mS cm^{-1} at 30°C) were measured as well as the mechanical properties (ultimate strength between 0.6 and 27 MPa at an elongation of roughly 53–87%). Swelling tests in aqueous methanol suggested good methanol tolerance.²²⁴ In a next step, the same group made clear that the conductivity and hydration are dominated by the extent of cross-linking of the membranes.²²⁵ In a further study, the polymer architecture was slightly changed by using norbornene as an additional co-monomer and, most importantly, ruthenium, nickel and cobalt bis(terpyridine) complexes were employed.

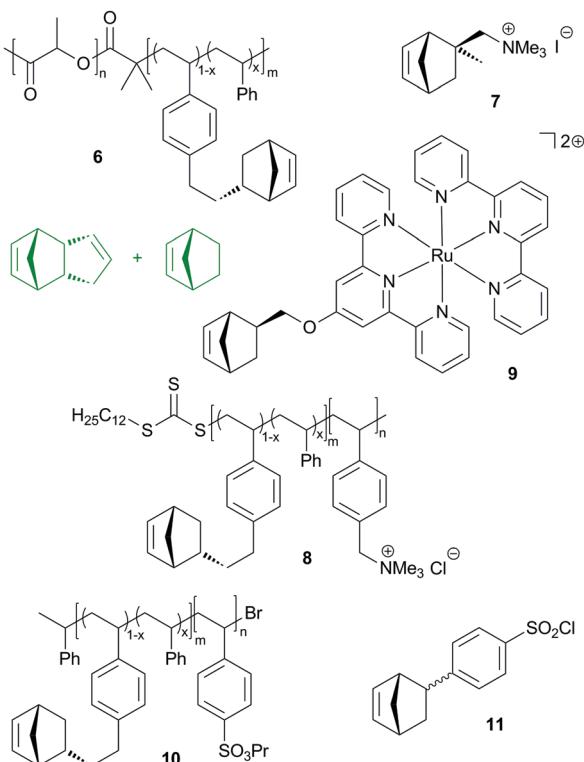


Fig. 9 Structural (in green) and functional (macro)monomers used for the preparation of nanoporous membranes.



While the water uptake, mechanical properties and chemical stability were greatly uninfluenced by the use of the different metal complexes, a high impact on conductivity was found. More earth abundant nickel was identified as a competitive alternative to ruthenium.²²⁶ This discovery was further investigated with the aim to explain differences in anion exchange membranes in general. Isothermal titration calorimetry was employed and indicated a weaker cation–counterion association in the case of the nickel complex.²²⁷

2.4.7. Proton exchange membranes. Amongst anion exchange membranes, also proton exchange membranes aimed at substituting Nafion® in *e.g.* direct methanol fuel cells were investigated. Macromonomer **10** was copolymerised with DCPD and/or cyclooctene and upon alkaline hydrolysis followed by acidification proton exchange membranes were obtained. They featured a bicontinuous morphology with continuous and size tuneable domains of the sulfonic acid phase and a continuous hydrocarbon phase. The latter phase provides the membranes' mechanical robustness and controls the swellability.²²⁸ The same membranes were also investigated for their ammonia selectivity *versus* nitrogen.²²⁹

More recently, benzenesulfonyl chloride bearing norbornene (**11**), DCPD and norbornene were copolymerized yielding upon hydrolysis 100–120 nm thick membranes. DCPD served as a crosslinker and increasing crosslinking decreased the proton conductivity, water uptake and swelling ratio, while the selectivity (proton conductivity *vs.* methanol permeability) increased with increasing crosslinking.²³⁰ Another group additionally incorporated carboxylic acid groups into the membrane.²³¹

In summary of this section, it can be stated that several highly promising nanoporous membranes based on DCPD have been disclosed. However, in the face of the high tendency of DCPD based porous materials to oxidize, their long-term performance is in question. Studies on the oxidation of nanoporous DCPD are definitely missing.

2.5. DCPD derivatives

In general, it is not easy to functionalise DCPD without compromising its polymerisability *via* ROMP and only two functionalized polymerisable DCPD derivative families have been disclosed so far (Fig. 10). The first example (12) is derived from heterodimerisation of carboxylated cyclopentadiene with cyclopentadiene. ROMP with G2 yields a linear homopolymer, which can be thermally cross-linked in a subsequent step. The cross-linked polymer exhibits glass transition temperatures higher than 170 °C.²³² Based on extensive studies, a radical process was identified to be responsible for the crosslinking reaction.²³³ The processability by RIM of the liquid monomer was demonstrated and similar storage and loss moduli to those for pDCPD were found.²³⁴

The other monomer family (13) is based on oxidizing the methylene group of the cyclopentene ring in DCPD. Initially, the acetylated monomer was reported in the polymerisation with G1 yielding a linear polymer characterized by higher glass transition temperatures but lower thermal stability when compared to pDCPD.²³⁵ Later, the parent alcohol, alkyl ethers and esters were polymerised (now with G2 in a solvent free variant) and the obtained cross-linked polymers were characterised *via* differential scanning calorimetry, thermogravimetric analysis and dynamic mechanical analysis.^{236,237} Generally, the polymerisation of the functionalised DCPD monomers is decelerated in comparison with DCPD. Taking the tedious preparation of both monomer types into consideration, weighty reasons for their application (instead of DCPD) are needed. Their main advantage might be their reduced volatility and smell with respect to DCPD. In some applications, the use of DCPD is limited because of its unpleasant odour.^{238,239} This issue might be resolved with functionalized DCPD derivatives.²⁴⁰

3. Challenges and perspectives

One of the main challenges in pDCPD chemistry and technology is, according to the judgement of the authors, to get control over the olefin addition based cross-linking at high temperatures. This process leads to steadily growing embrittlement and is particularly problematic in fibre based composite materials. The means to 'freeze' this process at a desired point (*i.e.* the desired cross-linking density) would be highly desirable. While oxidation seems not to be a big issue for many applications – in fact, the self-passivation of pDCPD is often rather an advantage – it has been ascertained as a core problem for many porous variants of pDCPD. Membranes and monoliths will drastically change their properties upon oxidation and will most probably lose their applicability. Although several examples of making use of oxidised porous pDCPD have been shown, the means to protect pDCPD from oxidising is desperately needed.

As regards initiators, gaining control over the stereochemistry of the double bonds and the tacticity with robust initiators is desirable. Additionally, initiators should be well soluble in DCPD, facilitating preparation. Photoinitiators operating in the visible at low loadings should be another target.

The fields of nanocomposites and fibre reinforced composites are going their way. Emphasis, however, should also be laid on finding cheap and practical solutions as soon as the principles are nailed down.

Frontal polymerisation of pDCPD is an emerging processing technology with great potential to revolutionise manufacturing. The same applies to the far less mature additive manufacturing processes not relying on frontal polymerisation. Fast stereolithographic fabrication of pDCPD parts would certainly spark great interest. Another emerging issue comprises research towards reprocessing of densely cross-linked thermoset pDCPD. Recently, a first study on the triggered degradation of pDCPD copolymerised with cyclic silyl ether-based monomers was uploaded to a preprint server. It is expected that the

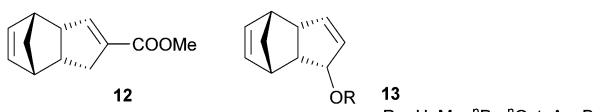


Fig. 10 Functionalised DCPD derivatives.

recyclability of pDCPD will attract increasing attention in the near future.²⁴¹

4. Conclusions

In recent years, it became clear that pDCPD can compete effectively with epoxy- and polyester resins in many applications. Thanks to the intense research work conducted in the last two decades, environmentally robust initiators and the means to adjust the pot life of resins became available. With this achievement, the design freedom of creating resins was greatly enhanced. The use of many co-monomers or fillers unimaginable to employ with conventional initiators became feasible and new processing possibilities emerged. pDCPD based micro- and macroporous materials with intriguing mechanical properties became accessible. Silica-reinforced nanocomposites emerged and fibre reinforced composites became accessible. The latter field of activity is of particular technological and economic interest and DCPD resins can now demonstrate their strengths. pDCPD is characterised by thermal and many mechanical properties which are comparable to competing resins but it shows a distinctly higher toughness. Its density is lower than that of many competing thermosets. DCPD-resins feature a low viscosity, allowing for faster and more flexible processing in consistently high quality. With the advent of new processing possibilities, such as frontal polymerisation or stereolithography, in the last few years, DCPD based resins offer another unique feature. Moreover, a company is advertising its DCPD technology with a considerably lower carbon footprint than epoxy resins. Although the underlying study for the claim has not been disclosed, the statement appears plausible.

Despite the tremendous discoveries and developments of the last decades, the authors are convinced that the real potential of pDCPD in materials chemistry is by far not uncovered.

Conflicts of interest

There are no conflicts to declare.

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