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Feature Article

The ROMP toolbox upgraded

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ABSTRACT

This article features the current state of research in olefin metathesis polymerization techniques towards the synthesis of functional polymeric materials. Emphasis is laid on work making use of ring opening metathesis polymerization (ROMP) initiated by ruthenium complexes published in the last five years. Other techniques such as alternating diene metathesis polymerization (ALTMET) are only covered when appropriate. A survey on polymer architectures accessible via olefin metathesis is presented and illustrated with manifold examples from research fields like life science, optics and electronics, sensorics or energy storage. Important new developments such as end-group functionalization or stereoselective polymerization are addressed. A chapter on using alternative and green solvents in ROMP is disclosed as well as an overview on the use of olefin metathesis polymerization using sustainable substrates. Applications in material science such as porous, liquid crystal or self-healing materials close the work.

1. Introduction

The present feature article intends to give an impression about recent developments in the sector of olefin metathesis polymerization. The number of corresponding publications has dramatically increased in the last few years and exceeded 200 in 2009. In 2004 we published a feature article summarizing principle aspects and the first boom about olefin metathesis after the invention of ruthenium based carbene initiators, thus providing a toolbox for ring opening metathesis polymerization (ROMP) [1]. With the introduction of 3rd generation Grubbs initiator (**G3**) in 2002 [2–4] new possible synthetic strategies emerged, widening the field for potential applications. Other than in metathesis reactions like ring closing metathesis (RCM) or cross metathesis (CM), polymerizations are above all performed with the commercially available catalysts Grubbs 1st, 2nd and 3rd generation (**G1, G2, G3**), Hoveyda 2nd generation (**H2**) or **M2** and **M31** [5] featuring an indenylidene instead of the benzylidene ligand (see Fig. 1). The dazzling array of different olefin metathesis catalysts and initiators has been reviewed recently [6]. Herein we discuss selected areas of metathesis polymerization in order to demonstrate the great capacity of this methodology, without claiming to be comprehensive. Emphasis is laid on latest tools provided to the olefin metathesis community and application-oriented work done in the last 5 years.

The last 5 years' research on olefin metathesis polymerization and in particular on ROMP has been focused on obtaining precision and diversity of macromolecular architectures (see Fig. 2). Regarding homo- and random copolymer synthesis, ROMP with ruthenium based initiators will convince the polymer chemist because of its paramount functional group tolerance. Furthermore, employing proper monomer and initiator combinations, living polymerization is feasible which allows for block copolymer synthesis almost without trade-off concerning the functionalities [7,8]. Chapters 2–4 will provide the reader with some examples illustrating the power of ROMP in this context. Starting with chapter 5 "End Group Functionalization" important steps towards precision are summarized. Nowadays several synthetic approaches for the preparation of telechelics are known which will facilitate the realization of almost any projected end-group. Chapter 6 will then show amongst other strategies the use of end-group functionalization for the preparation of grafted, dendronized and hyperbranched polymers. In short, combining ROMP with other polymerization techniques has become a vivid research area in the last five years.

A further step towards precision concerns the control of the stereochemistry of the polymers. This issue is highlighted in chapter 7 together with approaches to obtain alternating polymers with olefin metathesis polymerization. Chapter 8 and 9 deal with green aspects of ROMP as well as water soluble polymers and their application. Finally, chapters 10 to 12 are dedicated to latest development in porous and in self-healing materials as well as surface modifications based on ROMP.

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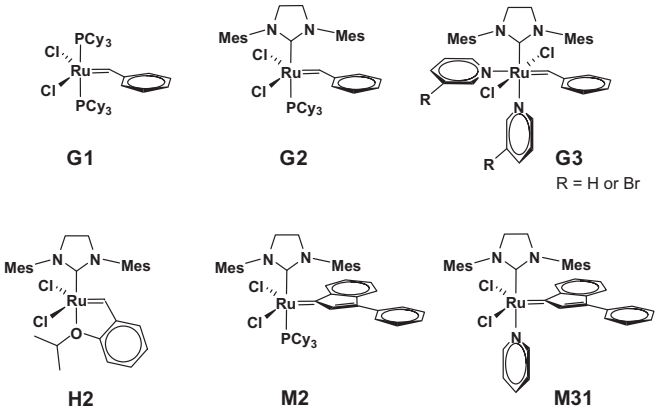


Fig. 1. Initiators used for olefin metathesis polymerization.

2. Homopolymers

In general, norbornene and its derivatives are typical monomers for ROMP. The high ring strain of about 27.2 kcal/mol [9] allows for efficient polymerization and substituents on the norbornene prevent secondary metathesis of the polymer backbone. Monomers with lower ring strain such as cyclooctene (7.4 kcal/mol) [9] can still be polymerized but chain transfer from secondary metathesis of the unhindered polymer backbone occurs during ROMP, which makes this and related monomer classes less attractive. Nevertheless it is to note, that under optimized reaction conditions living polymerization of other monomers than of a seven atom based bicyclo[2.2.1] architecture can be achieved. Grubbs et al. recently disclosed the living polymerization of *trans*-cyclooctene, which has a much higher ring strain (16.7 kcal/mol) than *cis*-cyclooctene [10]. Similarly, *cis*,*trans*-dibenzo[a,e]cyclooctatetraene could be polymerized [11]. Finally non-living ROMP of virtually strainless macrocyclic olefins is known as entropy-driven ROMP (ED-ROMP). A comprehensive feature article on this particular reaction has been published very recently [12]. Herein only selected applications of ED-ROMP are mentioned. In any case, the majority of work is done with norbornene based monomers as can be seen from the following examples.

ROM polymers exhibiting a pendant galactose glyco-group have been used as crosslinking agents for biologically derived extracellular collagen (Fig. 3) [13]. The so obtained hydrogel holds suitable physical properties for corneal tissue engineering, including optical transparency, appropriate elasticity, biological stability etc.

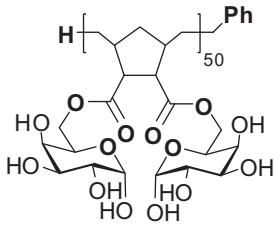


Fig. 3. Saturated ROM polymer with pendant glycol-group as cross-linking agent for collagen yielding hydrogels for corneal tissue engineering [13].

A nice showcase for the versatility of ROMP in the preparation of highly functionalized polymers is polynorbornenes carrying radical moieties. Such polymers find application as cathode active materials in organic radical batteries. Masuda et al. disclosed the synthesis of several norbornenes and 7-oxanorbornene based homopolymers featuring 2,2,5,5-tetramethyl-1-pyrrolidinyloxy- (PROXYL) [14] and 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) [15,16] moieties as their side chains. Related monomers were also employed in block-copolymer synthesis and their crossover chemistry was studied in detail [17].

Photosensitive ROM polymers bearing aryl esters or amides in the side chains which undergo the photo-Fries rearrangement upon irradiation with UV light were prepared. The photoisomerization reaction leads to the formation of aromatic hydroxyketones or aminoketones in the illuminated areas. Thereby the refractive index of the polymer film is drastically changed. Furthermore, post-exposure reactions can be performed and in combination with lithographic techniques, these post-exposure reactions can be used to prepare patterned functionalized surfaces [18–20]. Thus, such aryl esters can be regarded as protected hydroxyketones and illumination as protective group cleavage. In general, most functional groups do not impede the ROMP reaction and no protection is required.

Anyway there are some exceptions most importantly azides and alkynes are not compatible with ruthenium complex initiated olefin metathesis transformations and need protection. Recently, a protecting strategy for alkynes was presented by Tew et al. [21].

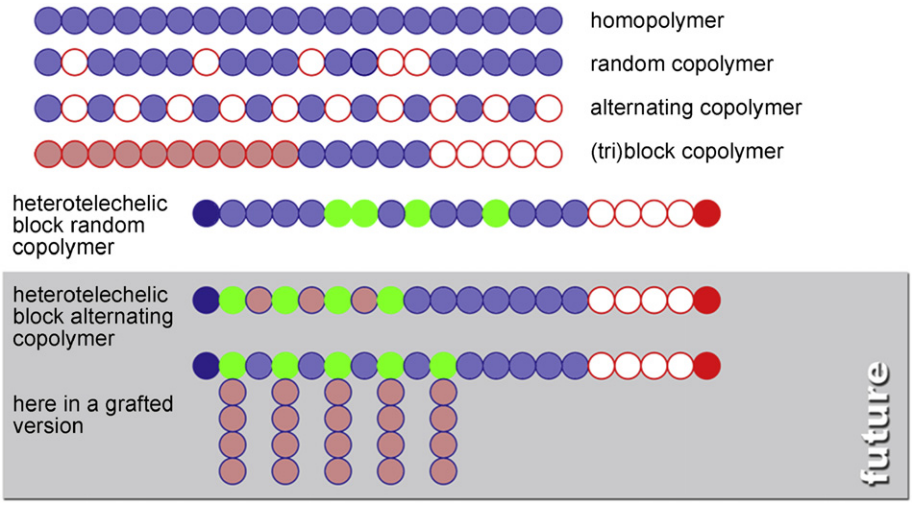


Fig. 2. The presence and the future of macromolecular architectures accessible via olefin metathesis polymerization.

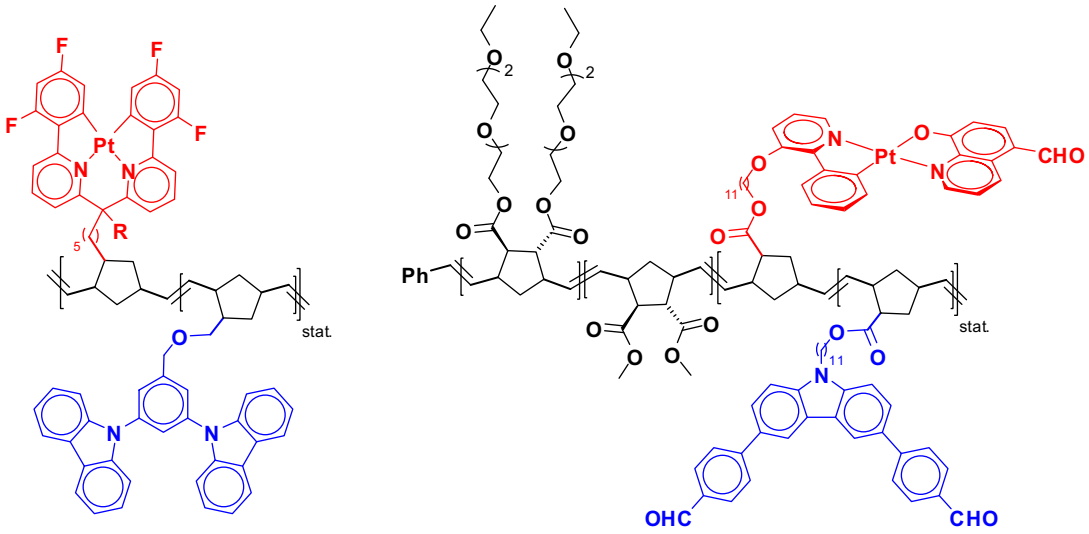


Fig. 4. ROM polymers for organoelectronics - host-guest-systems of Pt(II) complexes and carbazole moieties [46,47].

An oxanorbornene-imine monomer carrying a terminal alkyne moiety was protected by means of a dicobalt hexacarbonyl complex. This complex was found to be compatible with **G3** and easy to remove with ceric(IV)ammonium citrate. Well defined homo and block copolymers have been realized with this method. Alternatively, azides and alkynes are introduced in a post-polymerization reaction [22–24]. The acetylene and azide functionalities provide an interesting tool for further functionalization with "click" chemistry [25]. Polymer bound Cu-catalysts for click-chemistry and hydrosilylation have also been disclosed. In this case, norbornenes bearing NHC precursors were copolymerized and these groups were then converted to the corresponding copper complexes after polymerization [26]. Further examples of reactive groups for post-polymerization functionalization comprise aldehyde, ketone and maleimide functionalities [24,27], or α-chloroacetamide [28] and succinimidyl groups [29–31]. With the latter strategy polymers promoting cellular internalization were prepared [28–31] and a related substrate was used to prepare polymerizable gadolinium complexes, which are used as contrast agents for Magnetic Resonance Imaging [32]. Finally, a very special kinds of homopolymers should be mentioned. The so called polymeric ladderphanes consist of multiple layers of cyclophanes (formed before polymerization) which are then linked via at least two polymerizable tethers per cyclophane unit using ROMP [33].

3. Random copolymers

An application of ROMP derived random copolymers is the covalent incorporation of optical sensor moieties into a polymer matrix. ROM polymers have been tested as matrix materials for the oxygen sensing phosphorescent complex platinum tetrakis(pentafluorophenyl)porphyrin. A correlation between the nature of the ROM polymer's side chain and the optical response of the sensor molecules has been established [34]. Several works are dedicated to the synthesis of ROMP-able optical sensor molecules such as phenantroimidazoles [35,36], europium complexes [37] or xanthene dyes [38], their random copolymerization and the evaluation of their sensing profiles in the copolymers. Another application comprises random copolymers with covalently bound eosin and/or ethyl dimethylamino benzoate units which were tested as macroinitiators for the photopolymerization of acrylates aiming at an initiator/coinitiator system which combines good polymerization activity with improved migration stability [39].

Moreover, ROMP based materials found their application in the sector of organic electronics. For solar cell application new donor-acceptor materials were prepared by random copolymerization of phthalocyanine (Pc) and fullerene (C-60) bearing monomers. As evidenced by fluorescence quenching experiments copolymers exhibited a favourable photo-induced electron transfer, which was further confirmed by transient absorption spectroscopy [40]. A related work investigated nanowires made of ROMP derived block copolymers from zinc-porphyrin and C-60 bearing norbornenes [41]. Host-guest systems were also used as light emitting material in organic light emitting devices (OLEDs) and ROMP was used to copolymerize phosphorescent metal complexes based on platinum (II) [42] or iridium(III) [43–45] with properly selected hole conducting materials.

As an example, Weck et al. synthesized random copolymers with different ratios of the carbazole functionalized host monomer and the polymerizable guest complex (depicted in Fig. 4 on the left hand) [46]. A similar strategy was followed by Niedermair et al. to reduce aggregation of the phosphorescent dyes that would cause self-quenching of the phosphorescence and to obtain a large Stoke's shift. The random composition of this optical active segment was combined with an amphiphilc block copolymer architecture resulting in a triblock-random copolymer (see Fig. 4 right side) [47].

The polymer formed aggregates when dispersed in a selective solvent and energy transfer from the host to the guest occurred resulting in red phosphorescence. Addition of unselective solvents swelled or disrupted the aggregates as signalled by bluish green fluorescence of the host material. This example clearly shows the scope of combining the high functional group tolerance of ROMP and its living nature for the preparation of macromolecules with complex architecture for obtaining designed properties. This issue will be discussed in the next section.

4. Block copolymers and their structural diversity

Due to their advantageous polymerization manner (fast and living nature), 3rd generation initiators **G3** or **M31** establish easy access to well defined block copolymers with narrow molecular weight distributions. Polymers consisting of various blocks bearing different functional moieties will self assemble under selective conditions to give supramolecular structures such as micelles, liquid crystals or semi crystalline materials. Anyway, morphology control of polymeric materials is an important factor for literally all

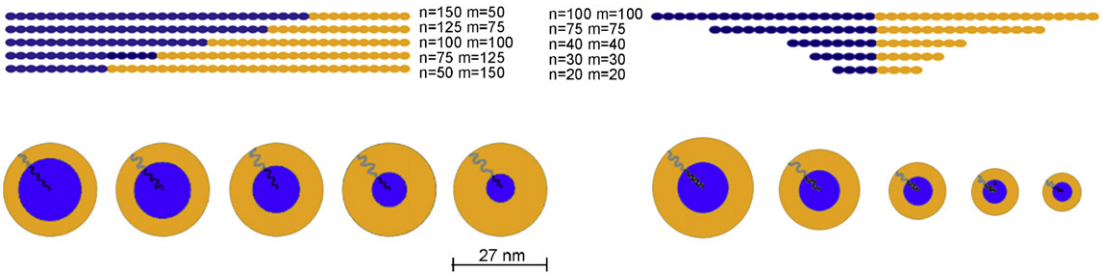


Fig. 5. above: Representation of the composition of amphiphilic block copolymers (n = repeating units of the hydrophobic segment, n = repeating units of the hydrophilic segment) and – below: representation of the size and architecture of the spherical micelles formed in a selective solvent. Redrawn from Ref. [48].

applications. The following showcase will illustrate the precision, which can be obtained when ROMP is employed for the preparation of block copolymers. Trimmel et al. prepared a series of amphiphilic block copolymers bearing carboxylic acid groups in the hydrophilic and dimethyl ester groups in the hydrophobic block by varying the overall chain lengths and the block lengths. The self assembly of those polymers was investigated in selective solvents by means of dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS) and authors found a good correlation of the size and the core-shell dimensions of the micelles with the polymers constitution (*cf.* Fig. 5) [48]. Later authors investigated the microphase separation of these polymers in the solid state [49] as well as the behaviour of the micelles upon changes of the pH value and the ionic strength of the selective solvent [50]. Furthermore, well defined block copolymers consisting of a long carboxylic acid bearing block segment and short polyhedral oligomeric silesquioxanes (POSS) bearing segment have been described [51].

The most important approach in block-copolymer synthesis is the sequential addition of the different monomers using an initiator suited for living polymerization. Additional functionalization of one or both of the polymer segments by randomly copolymerizing further monomers is also feasible. The triblock random architecture mentioned above is a good example for that and a sketch for such polymer architecture is given in Fig. 6. Examples for that polymer architecture were realized with pH-sensitive dyes like eosin and fluorescein [52,53] or with cinnamic acid derivatives allowing for light induced crosslinking of the polymer strands [54]. In the latter case, the photo crosslinking process was used to prepare nanoparticles upon illumination of micelles. A similar strategy was followed to obtain fluorine-18 functionalized nanoparticles which were aimed at using them as in vivo molecular imaging agents [55].

Photo crosslinking of micelles can also be achieved by using the reaction of multifunctional thiols with the double bonds of the polymers' backbone [56].

Another example for amphiphilic block copolymers was disclosed by Tew and Eren who used a phosphonate functionalized

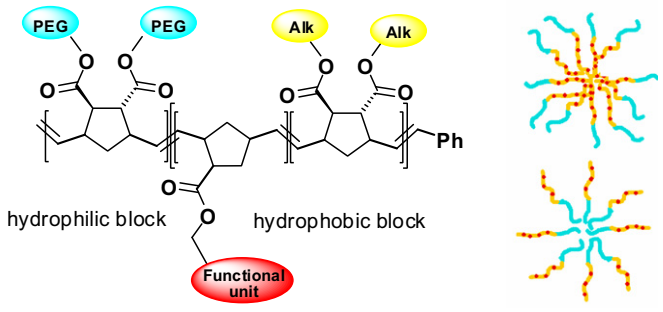


Fig. 6. left: example for a functionalized amphiphilic block-random-copolymer; right: micelle formation in polar and nonpolar solvent.

norbornene to copolymerize it with an alkylated substituted oxanorbornene monomer [57]. Transesterfication with TMS-bromide and hydrolysis yielded well defined amphiphilic block copolymer, soluble in THF-water mixtures. Phosphorous containing polymers are of great interest for their flame retardancy on the one hand, but also for biomedical applications due to beneficial adhesion properties to metals, bone and dental material [13].

Recent publications by Sanda and Masuda et al. impressively demonstrate the functional group tolerance of ROMP with 2nd and 3rd generation initiators. They synthesized amphiphilic block-copolymers from amino-acid substituted norbornene derivatives. The carboxy or the amino termini of the amino acids forming the hydrophilic segment were not protected in their approach [58]. The hydrophobic segment was also made from an amino-acid substituted norbornene derivative. In this case the terminal carboxy group was esterified. The described work follows several publications on polymerization of amino acid functionalized norbornene monomers, a topic which was elaborated by this group in recent years [59–64].

Also in organoelectronics ROMP derived block copolymers found their application. Swager et al. prepared a precursor ROM block copolymer functionalized with phenylene-thiophene or phenylene-furan moieties that will, in a second step form a conjugated and thus conductive network by electrochemical means [65]. The tendency of block copolymers to phase-separate is used to build up nano-structured conducting polymers. The monomers for the electroactive block used in Swager's case are norbornene derivatives with a two-point-fused substituted phenylene ring in order to align the conductive moieties along the initial backbone. The co-block is composed of norbornene or oxanorbornene ethers (see Fig. 7). A similar work describes the synthesis of nonconjugated copolymer precursors containing polymerizable triEDOT and nonpolymerizable diphenyl triEDOT at side chains with ROMP. These polymers were selectively cross-linked at the triEDOT moieties under oxidative conditions producing polymers exhibiting broad absorption signals [66].

In another approach, Swager uses ROMP copolymers in connection with carbon nanotubes (CNT) [67]. CNTs are highly quested in numerous applications due to their excellent electrical and mechanical properties [68]. By covalently binding an electroactive polymer comprising an ion conducting polymer block to the CNT, several challenges are mastered at once: The dispersibility of the CNTs in organic solvents is impressively increased, the need for high bulk conductivities on the part of the electroactive polymer is lowered due two backup of the CNT, and counter ion diffusion is enhanced thanks to the block copolymer architecture (see Fig. 8). Carbon nanotubes bearing covalently linked norbornenes were also used to enhance the toughness of polydicyclopentadiene in the corresponding composite [69].

Recently Turner at al. disclosed a strategy to prepare homo- and even block copolymers of fully conjugated *meta*- and *para*-phenylenevinylene type by ROMP of cyclophanediene-derivatives

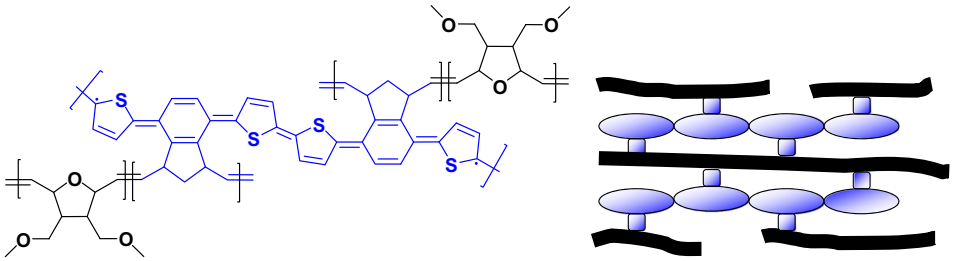


Fig. 7. Architecture of a conducting polymer with a ROMP derived backbone. Redrawn from Ref. [65].

[70–73]. A final example of the versatility of ROMP comprise the preparation of well-defined epoxy-containing block copolymer which stabilized in situ generated iron oxide (γ-Fe_2O_3) nanoparticles. The stable nanocomposite exhibited superparamagnetism at room temperature with high saturation magnetization [74].

5. End group functionalization

Polymers exhibiting exactly defined end groups are valuable tools in manifold applications in polymer science. In particular, proper end-group functionalization paves the way for combining different polymerization techniques such as RAFT (reversible addition–fragmentation chain transfer polymerization) [75,76] or ATRP (atomic transfer radical polymerization) [77,78] with ROMP in the preparation of block copolymers. Thus the structural diversity of accessible polymer architectures can be further enlarged (*cf.* next chapter).

Generally, the functionalization can be performed either on one chain end (semitelechelic) or on both chain ends (telechelic). Telechelic polymers can be classified into homotelechelics (equal functional groups) and heterotelechelics (dissimilar functional groups on each polymer chain end). The functional group can be implemented by (i) using a metathesis initiator bearing a functional carbene, (ii) using sacrificial synthesis or chain transfer agents during polymerization, and (iii) using a functionalized terminating agent.

(i) The use of functionalized initiators displays the most efficient way to receive 100% functionalization. Every initiated chain is ensured to carry the desired functionality [79]. Still, only semitelechelic polymers can be obtained. Moreover, new end groups can only be introduced by a newly designed catalyst, implicating a tremendous synthetic effort. Among the functional initiators described in literature examples for functionalized titanium, tungsten and ruthenium complexes have been described. Slugovc et al. reported on the synthesis of three fluorescence-labelled ROMP initiators utilized for homo- as well as for block copolymerization [80]. More examples can be found in a recent review [79]. In this context it has to be mentioned that functionalization of the initiator bears severe drawbacks such as the need of protection of some functional groups or, most importantly, changed initiation efficiency. The latter issue might disqualify the initiator for controlled living polymerization.

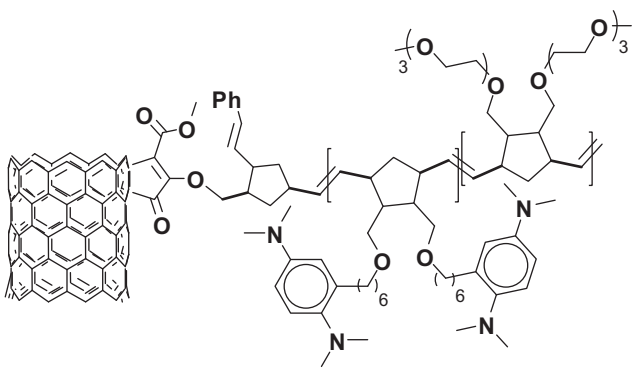
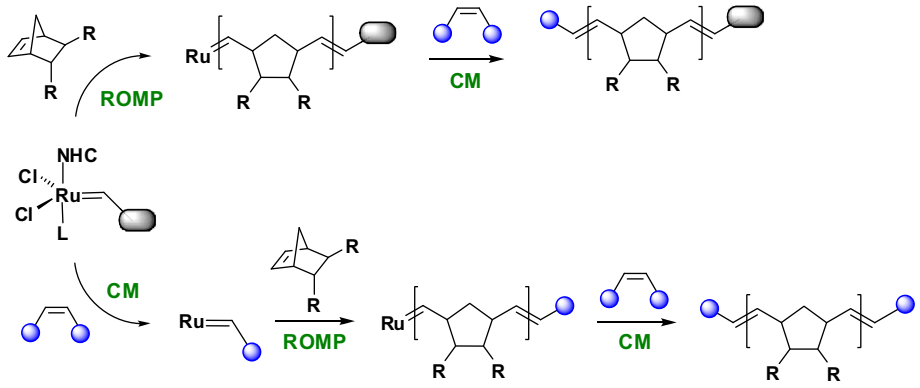


Fig. 8. Carbon nanotube covalently functionalized with a block copolymer comprising an electroactive and an ion conducting polymer.

(ii) Chain transfer agents (CTA) are usually acyclic internal olefins which undergo a cross metathesis reaction with the carbene of the growing polymer chain. Thus the polymer is cleaved off the complex and a new active species is formed, ready to start a new polymer chain. If the reactivity of the monomer is much greater than the reactivity of the used CTA, the reaction can be performed in a one-pot-synthesis [81]. Grubbs and coworkers tested various CTAs regarding their terminating capacity. The efficiency of the end-group functionalization varied between >90% and 40%. The best results were gained with sterically unhampered CTAs without any polar groups [82]. This strategy allows for monotelechelic as well as ditelechelic polymers depending on the sequence monomer and CTA are added (*cf.* Scheme 1). The average molecular weight is dependent on the stochiometrical ratio of monomer to CTA [79]. Reports concerning end-functionalization using CTA synthesized via ADMET (acyclic diene metathesis polymerization) [83] have previously been published. A cross metathesis of ADMET polymers and terminal olefins was performed to generate e.g. amorphous hydrophobic telechelic hydrocarbon diols [84] or silacyclobutane endcapped oligomers which were thermally chain-end cross-linked afterwards to give insoluble elastomeric materials [85].

Also the use of electron deficient olefins like acrylates displays another useful method for simple end-functionalization. Functionalization degrees ranging from 50 to 100% were achieved [86].

Sacrificial synthesis is not based on cleaving off of the initiator from the growing chain and can therefore also be employed to place the functional group at the beginning of the desired polymer chain. It represents a sophisticated route where a cleavable polymer block is polymerized after or before the required polymer. The attached block is then cleaved off the polymer chain by destroying it in a deprotection reaction liberating the desired functional group [79]. In the first reports 1,3-dioxepines were used to introduce hydroxyl-groups [87], followed by reports about the utilization of the corresponding sulphur analogs, namely 1,3-dithiepines [88]. The decomposition of the sacrificial polymer block is realized by acidic hydrolysis or hydrogenation in the case of dioxepines releasing “half a dioxepine” that is a hydroxyl group, at the end



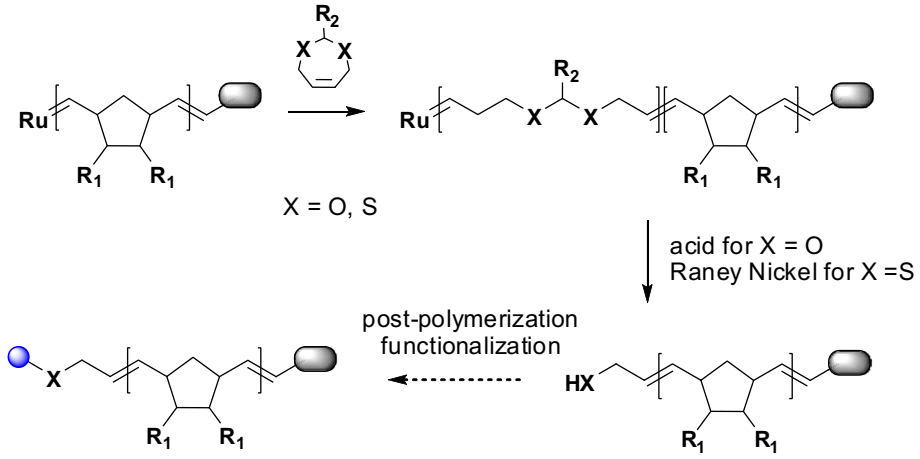
Scheme 1. Synthesis of telechelic and semitelechelic polymers using a chain transfer agent [79].

of the polymer chain. In case of dithiepines Raney nickel is used to liberate the desired thiol function (*cf.* Scheme 2).

Kilbinger et al. reported on the efficiency of various sacrificial monomers. In case the initiation rate of the sacrificial monomer is faster than the propagation, only a small excess of the corresponding monomer is necessary to achieve high degrees of functionalization [89]. In the very best case an equivalent amount of sacrificial monomer to initiator should be enough to functionalize every polymer chain. The synthesis of telechelic polymers via ROMP using sacrificial synthesis yields ABA or ABC triblock copolymers. If in an ABC triblock system A or C is a phenyl substituted dioxepine, it can be cleaved off separately by using Raney nickel. Hydrogenation with Raney nickel is known to remove phenyl acetals completely and leave deprotected hydroxyl-groups behind [90]. The formed hydroxyl group can then be functionalized individually before the other block is decomposed by acidic hydrolysis or hydrogenation. Thus the synthesis of heterotelechelic polymers is possible.

Another route to obtain homotelechelic polymers, namely the use of sacrificial multiblock copolymers was presented very recently by Grubbs et al. In place of triblock polymers, penta- or even heptablock copolymers were synthesized and subsequently hydrolyzed. The cleavage of all dioxepine units resulted in the formation of three or four polymer chains respectively, exhibiting almost monomodal weight distribution [90]. In this way a more economical approach to prepare ROM polymers was disclosed. A similar aim was targeted in a related study where conventional chain transfer agents such as 4-octene were used in a novel approach termed pulsed-addition ROMP (PA-ROMP). In PA-ROMP the CTA reacts almost exclusively with the living chain end, releasing a polymer strand and a regenerated initiator which can polymerize a subsequent batch of monomer. In this way up to ten subsequent polymerization cycles could be performed, each releasing almost the same polymer. This means, that the initiator amount could be reduced by the factor of ten. Block copolymer synthesis via PA-ROMP is also possible [81]. PA-ROMP will certainly be of high importance whenever commercialization of ROM polymers is targeted.

(iii) Terminating agents for ruthenium mediated metathesis have to contain olefinic or vinylic groups, other than for alternative transition metals like titanium, tungsten or molybdenum which also react with aldehydes, ketones and oxygen [79]. Usually termination aims for the creation of an electronically deactivated Fischer carbene that will suppress further metathesis reaction. The most commonly used terminating agents are vinyl ethers, plain ones like ethylvinylether for simple termination, and substituted ones for the implementation of special functional groups. According to literature a great diversity of functionalized vinyl ethers is known. Examples comprise fluorescein, biotin and azide [29] functionalized derivatives. The azide end-group afterwards was used to run an alkyne-azide click reaction. Unsaturated lactones such as vinylene carbonate (VC) and 3H-furanone (HF) are alternative quenching agents for ROMP. By using

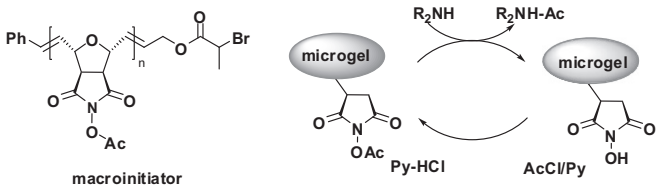


Scheme 2. Sacrificial synthesis of end group functionalized polymers [87,88].

those aldehyde and carboxylic acid end-groups can be introduced [91]. This approach was combined in another publication with sacrificial synthesis to prepare heterotelechelic polymers [92].

Very recently, Weck et al. reported on a supramolecular ABC triblock copolymer based on hydrogen bonding. The core unit consisted of a heterotelechelic polymer segment which was prepared by using a functionalized initiator and subsequent orthogonal end-group functionalization by a chain transfer agent. The introduced end-groups were the so-called Hamilton receptor at the initiator's site and 2,7-diamido-1,8-naphthyridine at the other terminus. Two additional polymer segments were mono functionalized with the complementary hydrogen bonding moieties, one of them using ROMP followed by the use of a properly substituted termination reagent. In solution, the supramolecular block copolymer formed (*cf.* Fig. 9) [93]. Related work precedes this report [94–96].

A current example for applying end-functionalized ROM polymers comprises the fabrication of microgels that are used as polymer supported acylation agents for amines in pharmaceutical synthesis [97]. An oxanorbornene based monomer bearing an activated acyl group was polymerized with **G2**. This was followed by end-group functionalization with an α-bromoester group to yield a suitable ATRP-macroinitiator. Radical polymerization with styrene and divinylbenzene gave cross-linked high molecular weight polymers that still retained solubility in THF. The so obtained microgel supported acylation reagents can be recovered after use (see Scheme 3).



Scheme 3. End group modified ROM polymers as macroinitiators for ATRP-derived functionalized microgels.

6. Grafted, dendronized and hyperbranched polymers

Macromolecular modification other than within the backbone can be accomplished by a grafting process. Graft copolymers have been designed and realized in many ways in order to achieve supramolecular structures that, in comparison to self-assembling block copolymers exhibit a more precise nanoscale morphology in each dimension [98,99]. This allows for high-end applications like impact resistant plastics, antifouling coatings [100] thermoplastic elastomers, compatibilizers or emulsifiers [101]. Three synthetic routes can be differentiated: (i) "grafting onto": attachment of ready side chains to ready backbone; (ii) "grafting through": homo- or copolymerization of macromonomers exhibiting side chains; (iii) "grafting-from": side chains are polymerized from the ready backbone. Depending on the strategy, different polymerization methods and their combinations (radical, metathesis) have been employed to achieve well defined brush copolymers [102]. Particularly the combination of atom transfer radical polymerization (ATRP) and ROMP has often been used [103–105]. In these cases, a norbornene backbone was polymerized by means of ROMP, before side chains like poly (acrylic acid) or polystyrene were grafted by ATRP. Fontaine et al. instead used a 3,4-difunctionalized cyclobutene to first initiate ATRP and afterwards use the resulting macromonomer in ROMP with **G2** which resulted in polybutadiene-*g*-(polystyrene-*b*-poly(acrylic acid)) [106]. Still, it was necessary to use drastic conditions for ROMP (70 °C, 76 h) and monomer consumption remained incomplete at a monomer:initiator ratio of 10. Cheng et al. synthesized a grafted polymer comprising intrinsic secondary structures within the side chains and therefore introduced another dimension of structural organisation of a polymer [107]. Norbornene-carboximide monomers comprising a TMS-protected amino functionality was successfully polymerized with **G3** applying a monomer:initiator ratio of up to 130. Previous attempts to polymerize the unprotected monomer had failed. The resulting "prepolymer" was then subjected to a controlled type of NCA (amino acid N-carboxyanhydride) ring opening polymerization, to achieve polypeptide grafts [108,109]. The synthesized graft polymers exhibited low PDI values and molecular weights close to the expected [107].

A mixed "grafting-through-grafting-from" approach with a sophisticated macromonomer was followed by Xie (see Scheme 4). He used a hetero-difunctionalized norbornene to implement two initiating sites: a hydroxyl group to initiate ROP of ϵ-caprolactone

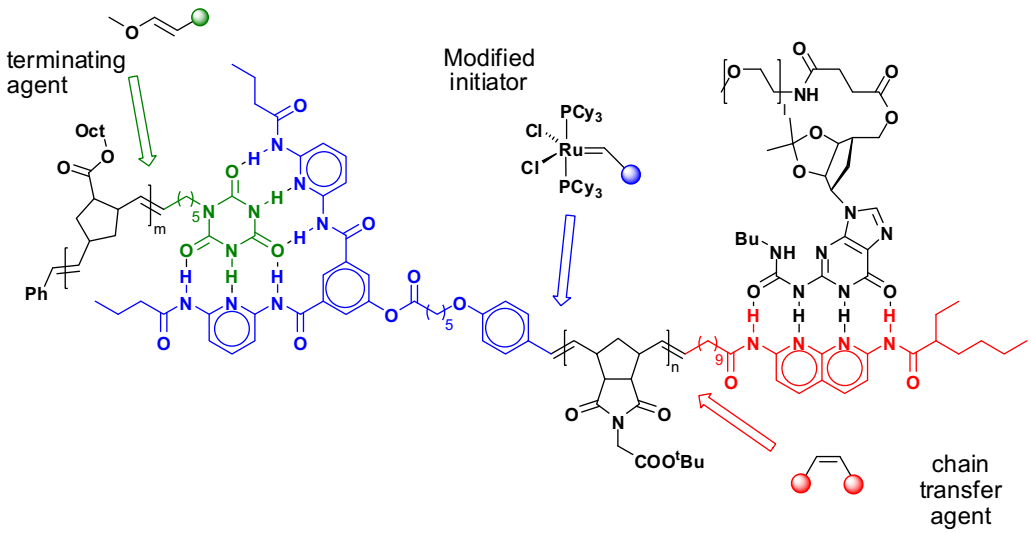
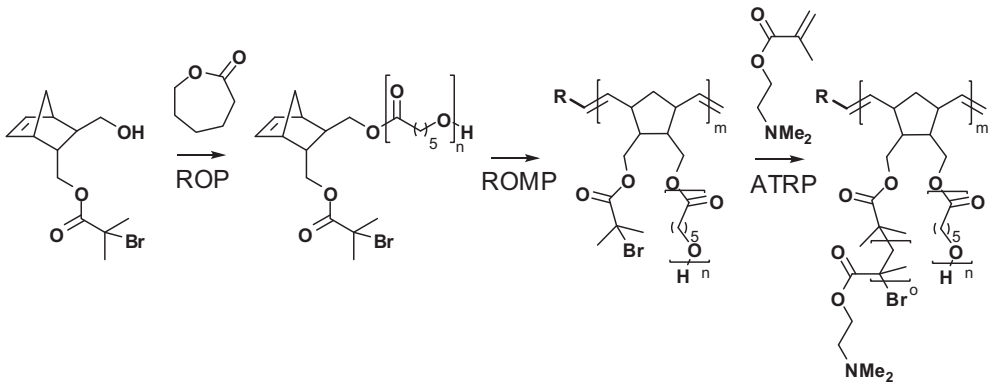


Fig. 9. Supramolecular ABC triblock copolymer and the key-steps of its preparation.



Scheme 4. Brush copolymer exhibiting high grafting density of amphiphilic side chains by combination of ROP, ROMP and ATRP [110].

(branch A) on the one hand, and a 2-bromoisobutyryloxymethyl group as ATRP initiator branch B [110]. It is to note, that polymerization of macromonomers like those described above is not easily accomplished. High amounts of initiators have to be used to achieve full conversion and living polymerization is often not feasible.

Kiessling published a new "grafting-from" strategy by exclusively using ROMP. Therefore she used a norbornene monomer with a pendant "dormant" grafting site, a maleimide [111]. After oligomerization with **G3** the maleimide function is transformed via a Diels–Alder reaction to give the corresponding norbornene moiety. The oligomers bearing polymerizable side chains where then reacted with norbornene derivatives featuring a α-chloroacetamide group. Depending on the ratio of this second monomer and the initiator **G3**, the grafting density could be roughly controlled. Homopolymerization of the second monomer is limiting the grafting process. However, polymers with a graft density up to 26% could be synthesized without formation of homopolymers of the second monomer (cf. Scheme 5) [111].

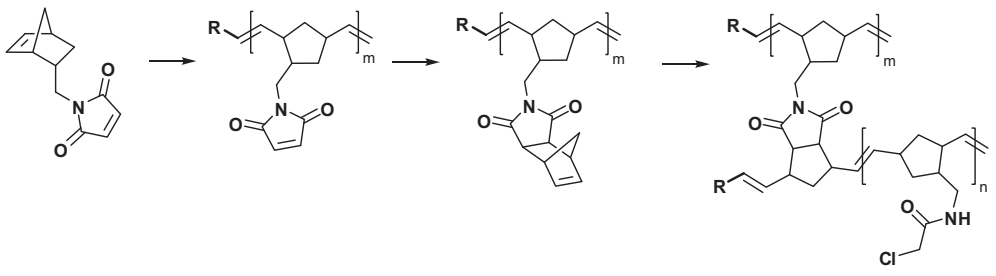
A mixed RAFT-and-ROMP "grafting through" strategy towards molecular brushes, taking advantage of the high activity of **G3**, is presented by Wooley et al. A norbornene-substituted RAFT chain transfer agent was used to polymerize *tert*-butylacrylate in a controlled manner. The macromonomer was then subjected to ROMP and the desired brush polymers were isolated in high yields with low polydispersities [112]. Similarly, norbornenes bearing polylactide and poly(*n*-butyl acrylate) substituents were used to prepare narrowly dispersed brush block copolymers as well as random copolymers [113].

Graft polymers are also realized by metathesis polymerization of linear dienes via ADMET, as published by Meijer et al. [114]. His approach also differs from others discussed above by the way of grafting. The grafts are not attached covalently, but due to quadrupole hydrogen bonding between 2,7-diamido-1,8-naphthyridines in the backbone and a substituted urea-pyrimidine derivative (*cf.* Fig. 10). Complexation of the 2,7-diamido-1,8-naphthyridine moieties is necessary for the polymerization to proceed and the urea-pyrimidine derivative can be regarded as a non-covalent protecting group. Further chemistry relying on olefin metathesis derived macromolecules and non-covalent interactions comprise work of e.g. Binder [22,23] and Weck [93–96,115,116], who also disclosed an account on this topic [117].

Grafted polymer structures have also found their way to medicinal applications. Emrick and Breitenkamp used a substituted cyclooctene backbone with grafted pentalysine branches and PEG chains in a "grafting through" approach. The resulting cationic amphiphilic copolymer was successfully used as DNA delivery vector for the transfection of COS-1 and HeLa cell lines. The encouraging results are related to the comb like structure of the polymer [118,119].

Due to their inherent self-organised structure dendrimers have been subject of smart material research like catalyst support, optoelectronics or biosciences [120]. Dendronized polymers generally exhibit a linear backbone with attached dendron side groups. The decoration of unsaturated polymer backbones with dendron units was found to be crucial for a shape persistent polymer chain (rod-like polymer) [121] Synthetic strategies resemble those for graft polymers (see above). Due to its versatility, ROMP has also been used for (mainly) the "macromonomer strategy". Therefore, norbornene derivatives have been equipped with dendrons of different shapes to be polymerized with **G2** or **G3**. A review done by Frauenrath in 2005 summarizes different approaches in that matter [120].

More recently, Fréchet et al. made use of ROMP as most suitable tool for the synthesis of block copolymers and synthesized a dendronized diblock-copolymer exhibiting two differently sized and functionalized dendrons (*cf.* Fig. 11) [122]. Despite these examples of meaningful use of metathesis polymerization with



Scheme 5. ROMP from ROMP graft copolymers.

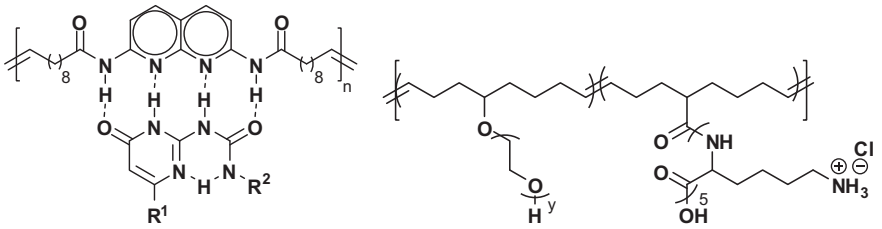


Fig. 10. left: ADMET polymer with variable graft, attached via H-bonding [114]; right: amphiphilic graft polymer including a pentalysine graft for gene transfection [118].

dendrimers, one has to establish, that until today metathesis has played a rather marginal role in dendrimer chemistry.

Non-dendrimeric, hyperbranched polymers have some advantages over the previously discussed dendronized polymers. Preparation is less complex and therefore more economic, hyperbranched structures can exhibit a large number of various functional groups and in many cases the "perfect" alignment of dendronized polymers is not required after all. Hyperbranched structures have been synthesized for example by means of ROMP or ADMET polymerization with an $AB_{n\geq 2}$ monomer [123]. Xie et al. used this approach and first synthesized a trifunctional AB_2 monomer comprising photoresponsive azobenzene as a core, two acrylate end groups and one terminal olefinic end group. Together with a suitable catalyst (**G2**), this gives a perfect ALTMET (alternating metathesis polymerization) [124] set. As electron-poor acrylates hardly homopolymerize, a high degree of branching is guaranteed (see Fig. 12, right) [125]. A completely different approach was followed by Kilbinger et al. who recently published the polymerization of acetal protected dihydroxy-norbornene derivative. Quenching with 3*H*-furanone led to carboxylic chain ends. After deprotection, the resulting multifunctional polymer chains connected and formed long chain branched polymer networks (see Fig. 12, left) [126].

7. Stereo- and sequence selective ROM polymerization

Controlled polymerization comprises not only the monomeric composition within the chain (copolymer, block-copolymer) but also the stereochemistry of the monomer units towards each other.

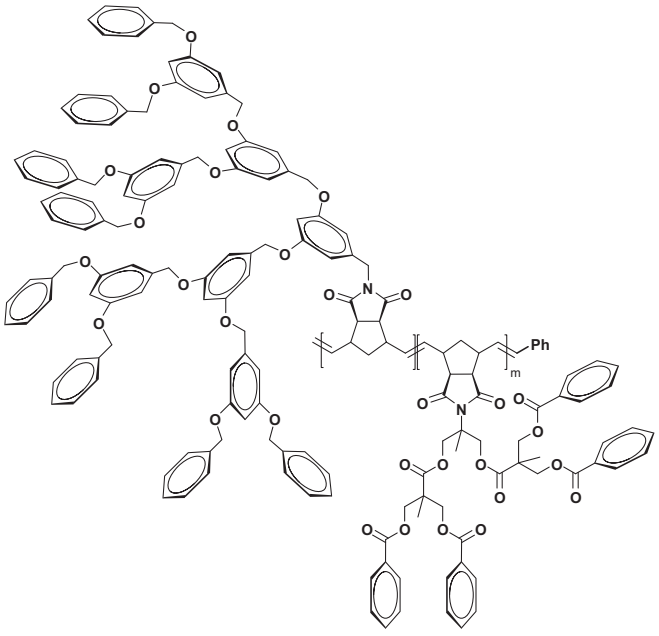


Fig. 11. Dendronized Diblock Copolymer.

As for norbornene derivatives that represent the most frequently used ROMP monomers, a whole bunch of possible configurations arise from the bicyclic structure and its various functionalization patterns: (i) *cis*/*trans* of the exocyclic double bonds, (ii) configuration of the allylic bridgehead-carbons (RS–RS, RS-SR) and (iii) linkage of unsymmetrically substituted monomers (head–head, tail–tail, head-tail, tail-head) [127,128]. Gaining control over the microstructure of a ROM polymer is still an issue of intensive investigations due to a lack of reliable, robust initiator systems. Transition metals such as molybdenum, tungsten, osmium or iridium have been used for stereoselective metathesis polymerization [129,130]. Some well defined molybdenum based catalysts that show highly stereoselective behaviour have been introduced by Schrock, Hoveyda et al. during the last years [131,132].Recently a *cis*-selective molybdenum catalyst was introduced featuring a hexaisopropylterphenoxide and a monopyrrolide ligand. Norbornadienes as well as cyclooctene derivatives were polymerized and yielded *cis*-polymers almost exclusively [133]. However, these systems suffer from high sensitivity towards moisture and oxygen making them inconvenient for practical synthesis. Up to now, stereoselectivity could not be satisfyingly realized with ruthenium based initiators. Noels et al. investigated a bimetallic $[RuCl_2(p\text{-cymene})]_2$ pre-initiator system that is activated by TMSD (trimethylsilyldiazomethane) and achieved polymers exhibiting a *trans* content of more than 90% (see Scheme 6). If the free coordination sites at the ruthenium centre can be accessed by a monomer in a bidentate manner, high stereoregularity is obtained. In contrast, if this coordination is inhibited by sterically demanding substituents on the monomer or by ligands such as phosphines competing for the vacant coordination site, sterical control is lost. The same goes for monomers that do not exhibit the possibility for bidentate ligation [127]. Still, the described system has some severe limitations. Firstly, an activator is required to get the active carbene species. Secondly, the rate of activation, that intrinsically determines the molecular weight distribution, is hard to control. Finally, stereoregularity can only be achieved with selected monomers.

A different degree of selectivity in metathesis polymerization was achieved by the realisation of strictly alternating ROM copolymers. Alternating preference towards two monomers is generally hard to achieve by a ROMP initiator due to an assumed lack of selectivity for the monomer's double bonds. Blechert and Buchmeiser et al. modified the NHC ligand of a Grubbs initiator in order to gain such selectivity. One of the mesityl groups was exchanged for the more bulky phenylethylgroup. This modification allowed for the alternating polymerization of cyclooctene and norbornene, which was explained by different insertion rates for norbornene and cyclooctene in dependence of the monomer inserted just before (*cf*. Fig. 13) [134]. A more detailed study including several new inititiators bearing modified NHC ligands was issued shortly afterwards [135].

Alternating copolymerization of cyclooctene and norbornene was pioneered by Chen et al. using chelating phosphine co-ligands [136,137]. It is to note, that most of the initiators developed for alternating ROMP showed different *cis*/*trans* selectivity when

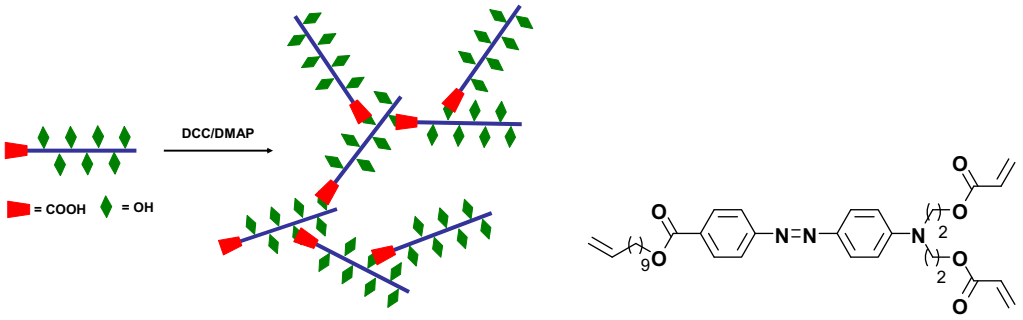


Fig. 12. left: Branched polymers [126] right: trifunctional ALTMET-monomer for photoresponsive hyperbranched polymers [125].

compared to the selectivity obtained from standard initiators (*cf.* Fig. 1). An isolated but elegant example for alternating copolymerization of two amino acid functionalized norbornene derivatives was disclosed by Sanda et al. (see Fig. 14) [64]. Most likely, a pre-organization of the monomers is the reason for the control of the polymer sequence.

Another example of stereoselective polymerization of an enantiomerically pure amino acid based norbornene monomer was published by Buchmeiser et al. A polymer featuring an all *trans*-structure was obtained [138].

An approach with a related aim – to increase precision of the macromolecular architecture – was introduced by Wagener. He demonstrated the convenience of metathesis polymerization techniques in the synthesis of functionalized polyethylenes. With ADMET the space, i.e. the length of the polyethylene segment between the functional groups, can be precisely determined by using properly substituted α,ω-dienes (*cf.* Scheme 7). Hydrogenation of the polymers finally gives functionalized polyethylene. Materials prepared with this strategy were termed precision polyethylene. On the other side an intended "pseudo-random" placement can be accomplished via ROMP and it has been shown that precision polyethylene have distinctly different physical properties when compared to irregular counterparts prepared by ROMP [139].

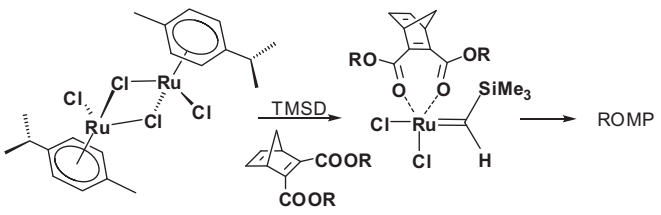
Precision polyethylene bearing ionic liquids [140], bioactive moieties [141], alkyl groups [142], polyethyleneglycol groups [143] or halides [144] to name some recent examples were disclosed.

8. Unusual solvents and water

Usually ROM polymerization is carried out in solution of organic solvents. Alternatively bulk polymerization or polymerization in a heterogenous system can be accomplished. The type of solvent drastically affects the reaction. Most importantly monomer, initiator and the generated polymer have to be soluble in the chosen solvent when controlled polymerization is aimed at [1]. Apart from that, the solution media can be picked according to the desired conditions. Recently some alternative solvents for ROMP have been explored.

Ionic liquids (IL) have already proved their value as solvents for various applications for transition metal catalyzed reactions because they dissolve organometallic compounds. The term ionic liquid refers to a liquid that exclusively consists of ions. The main difference between an ionic liquid and a molten salt is the low melting point, as ILs are already liquid at or near room temperature (melting point $<100\ ^{\circ}C$) [145]. Advantageous features such as non-flammability, facile recoverability, negligible vapour-pressure and high thermal stability make them to "green" alternatives for conventionally used organic solvents [146]. Regarding metathesis, many reports of ILs for (RCM) [147–149] and CM were published, whereas publications about ROMP in ionic liquids are still rare. The very first report of this kind of reaction was published in 2002 [150].

In order to evaluate the influence of the IL design on the metathesis reaction, the Buchmeiser et al. performed several polymerization reactions using a model monomer, **G3** and various ionic liquids. The results showed that ILs based on strongly bound counteranions such as halides or nitrates do not allow any polymer formation, whereas more weakly bound anions (BF_6^-, PF_6^-) yield high molecular weight polymers. The polydispersity index (PDI) is also influenced by the nature of the IL. According to NMR studies, ILs interact with the initiator applied and thus the formation of any polymer is inhibited [151]. Xie and co-workers explored the influence of ionic liquids on the polymerization of functionalized cyclooctenes. The reaction was carried out once in CH_2Cl_2 and once in the IL $[1\text{-Me-3-BuI}]^+PF_6^-$ at 30 °C. In the IL, markedly improved control over molecular weight and PDI was achieved. With 5-hydroxy-1-cyclooctene higher conversion over the time and lower PDI values (below 1.4) were obtained [152]. Summarizing it can be said, that ILs are a good alternative to perform selected ROMP reactions, but no general recommendation can be given to date.



Scheme 6. Activation of cymene precataylst for stereoselective ROMP.

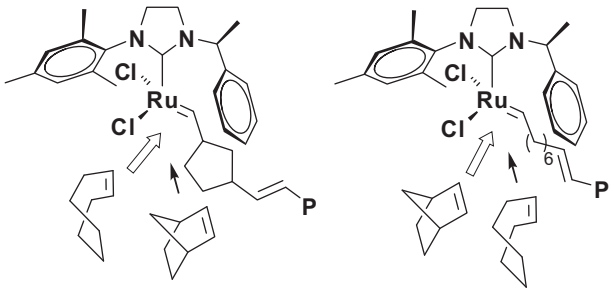


Fig. 13. Steric control in alternating ROMP.

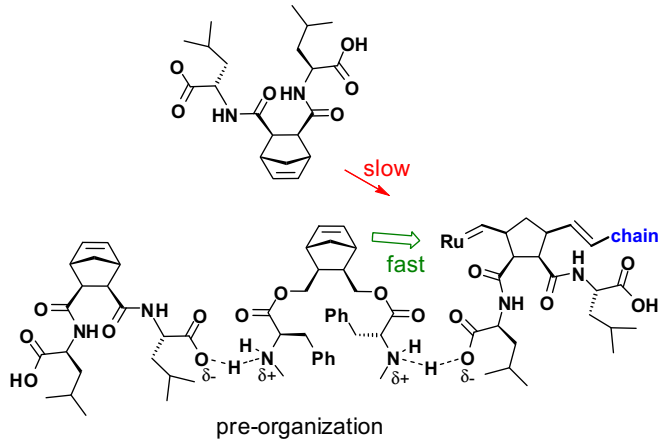


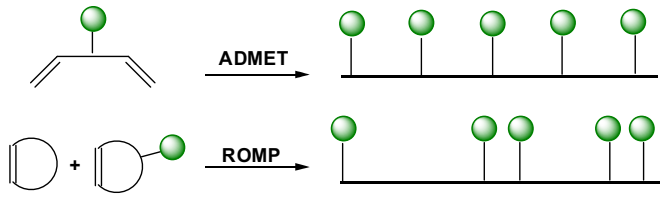
Fig. 14. Supramolecular pre-organization for alternating ROMP.

Recently a report about D-limonene as solvent for a ROMP reaction was published. The authors carried out several ROM polymerizations in D-limonene leading to similar results as gained in polymerizations performed in toluene. Interestingly, the SEC revealed a lower molecular weights than for the corresponding reaction in toluene. A possible explanation for that are chain transfer and chain degradation reactions because of the unsaturated nature of D-limonene [153]. Furthermore, metyl decanoate [154] and dimethyl carbonate [155] were evaluated as solvent for RCM and cross metathesis. Lowe et al. established a 1:1 mixture of 2,2,2-trifluoroethanol (TFE) with dichloromethane for the polymerization of cationic oxanorbornenes and zwitterionic betaines [156]. The implementation of this new solvent leads to an alleviated synthesis of ionic polymers with commercially available initiators without any modifications at the catalyst or the monomer. The polymerization occurred in a living manner [157,158].

The use of water as a reaction solvent has emerged as a subject of increasing interest due to environmental issues. Also the methodology of olefin metathesis in all its variations has been investigated regarding its appropriateness for aqueous synthesis and review on olefin metathesis in water has been issued [159]. The first ROM polymerizations of oxanorbornenes carried out in water, were performed using simple ruthenium salts such as $[Ru(H_2O)_6(tosylate)_2]$ [160–162]. However these Ru salts did not polymerize in a living manner and due to inefficient initiation yielded erratic polymers. The first report about a successful aqueous polymerization of NBE with a ruthenium carbene initiator was published by Grubbs in 1996. However, yields were low and the obtained polymers are characterized by broad molecular weight distributions. These effects were explained by the insolubility of the initiator in water. Further experiments with hydrophilic respectively hydrophobic monomers by means of a cationic emulsifying agent (dodecyltrimethylammonium bromide (DTAB)) were performed. Both monomer classes could be in principle polymerized but a small amount of organic solvent was necessary in all cases to achieve polymerization [163]. Another approach for ROMP in aqueous media is the implementation of microemulsions [164–170]. A hydrophobic initiator is dissolved in a minimal quantity of organic solvent (e.g. toluene). The organic phase forms nanodroplets in the aqueous phase, stabilized by a surfactant. The emulsion of the organic media, water and surfactant becomes colloidally stable after adding a co-surfactant (e.g. hexadecane) and a suitable treatment (sonification, microfluidization). The droplets size ranges normally between 100 and 400 nm. The emulsion is then set into contact with the certain monomer, which diffuses through the aqueous media to the initiator droplets and the polymerization can start [171]. The resulting polymers possess a particle shape, not always similar to the size of the droplets caused by monomer diffusion and/or Ostwald ripening [176]. Various derivatives of norbornene and cyclooctene have been polymerized using miniemulsion polymerization. Yield increased with increasing amounts of organic solvent used for the droplet phase. High conversions within short times were achieved however the resulting polymers were often prone to flocculation [172].

To circumvent solubility problems with the initiator, water-soluble metathesis initiators were synthesized. The first complexes disclosed were **G1** derivatives and even if they initiated the polymerization in a well-defined manner, the initiators were unstable in the aqueous media and the propagating species decomposed before the reaction was completed [173,174]. Some years later, the first 2nd generation water soluble complex featuring a PEG substituted unsaturated NHC ligand was presented [175]. The initiator catalyzes ROMP, albeit in ineffectual time, but shows limited activity for other metathesis reactions carried out in aqueous media. Upon the addition of 1 equiv. of HCl, the polymerization activity of **WS1** (*cf.* Fig. 15) is enhanced dramatically, thanks to protonation of the free phosphine by the acid inhibiting the re-association of the phosphine ligand to the ruthenium centre. Another PEG substituted derivative **WS2** in this case a phosphine free **H2** analogue was published. It showed increased activity in ROMP, RCM and CM compared to the phosphine containing catalysts, supposedly also because of the more active saturated NHC [176]. The activity of the cationic Hoveyda derivatives **WS3** and **WS4** are similar to the activity of **WS2** [177]. Furthermore a water soluble **G3** analogue bearing PEG-substituted pyridine ligands has been disclosed [178].

Successful polymerization in water is closely related to the solubility of the polymers themselves. Water-soluble polymers



Scheme 7. ADMET and ROMP for morphology tuning of poly(ethylene-co-acrylic acid) copolymers [139].

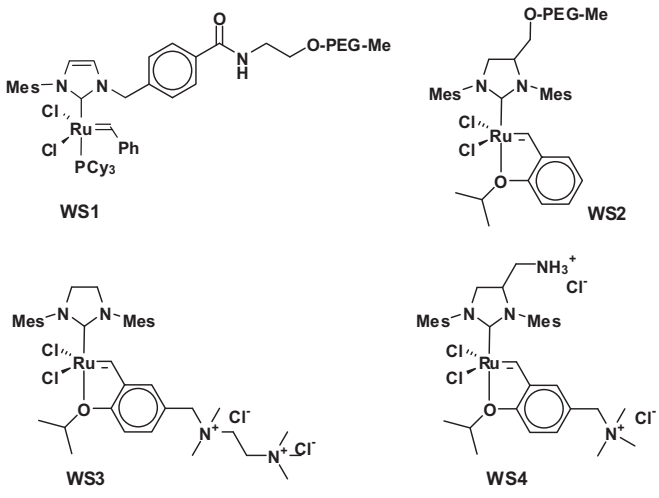


Fig. 15. Water soluble catalysts for aqueous ROMP.

have been the subject of intensive research over the last years. These polymers are of great interest in industry and academia due to their potential applications in drug delivery, biomaterials and many areas of soft materials. The most frequently used strategy is functionalizing norbornene moieties with a variable number of ethyleneglycol/ethyleneoxid (EG/EO) units. While some authors relate solubility to samples, in which the dissolved polymer persists as a single chain, others define micelles that lead to clear solutions as dissolved. Reported numbers of required EG units ranges from long side chains with 44 or 25 units [179], to shorter side chains with only two to seven ethyleneglycol moieties [180,185]. All these EG substituted polymers exhibit certain water solubility and in every case clear solutions were obtained after the exposure to water. Recently other strategies for the synthesis of water-soluble polymers were published using acid [181]- or amine functionalized norbornenes [182] and norbornene based polybetaines [183]. In spite of their dissimilarities in structure all polymers resulted in clear solutions when dissolved in water. Nevertheless dynamic light scattering tests were performed in some cases to investigate whether the solutions still contained aggregates. Regarding the amino functionalized polymers the aggregated part is negligible. In contrast, the acid functionalized polymer showed significant aggregation, even after the addition of salts or changing the pH [181]. On the other hand, acid functionalized polynorbornenes are soluble in alcohols [48].

Polymeric betaines contain both anionic (sulfonate, carboxylate, phopsphonate) and cationic (ammonium) functionality on the same repeating unit, ensuring the neutral charge of the polymer [183,184]. One of the most interesting features of polymeric betaines is the antipolyelectrolytic effect: The polymer is insoluble in pure water but becomes soluble upon the addition of small amounts of salt (eg. NaCl). Due to their general biocompatibility such materials are intensively explored regarding applications in the field of medical diagnostics, drug delivery or tissue engineering. Recently, ROMP has been used to synthesize well defined polybetaines using either **G1** [183] or **G3** [156].

A thermo responsive behaviour, the LCST effect (lower critical solution temperature) was found for water soluble PEG functionalized polymers [185]. It turned out, that the LCST effect is maintained within block copolymers that will form micelles. Also elastin-like polymers (ELP) show the LCST effect and, therefore, establish application possibilities in drug delivery or tissue engineering issues. ELPs are mimicking the natural connective protein elastin and comprise amphiphilic oligopeptide chains. As for ROMP, norbornene monomers with an oligopeptide side chain are usually hard to polymerize due to deactivation of the ruthenium catalyst by primary or secondary amines. However, Setton et al. managed to produce elastin-like low-molecular weight oligomers bearing amphiphilic decapeptide chains with **G2** at 0 °C [186]. A recent work uses PEG substituted amphiphilic block copolymers bearing folate and dye conjugates for targeting of tumor tissue. A particular result of this work is that osmium catalyzed dihydroxylation of the double bonds present in the polymers backbones led to significantly lowered critical micelle concentrations [187]. Similarly, Nguyen et al. used PEGylated block copolymers for drug delivery [188]. Another approach to obtain water soluble polymers was chosen by Kane et al. who first produced a non-water-soluble polymer which was then functionalized with hexylethyleneglycol amine to achieve water solubility [189] Fig. 16.

A special class of water soluble ROM polymers are those having biocidal properties. Materials active against pathogens like bacteria, fungi and viruses have gained importance in many fields such as food packaging or medical facilities. As for the boosting industrial need for this substance class, an economic way for the production of large quantities thereof is required. Within the last

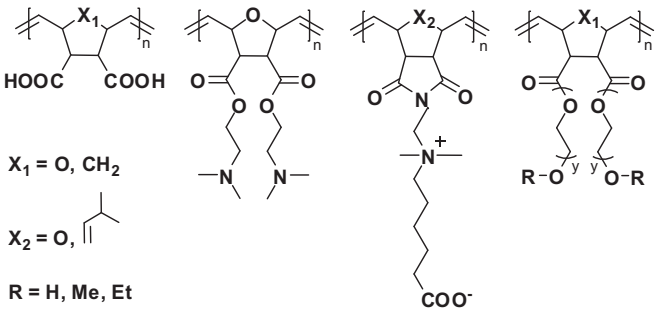


Fig. 16. Examples of water-soluble polymers.

decade huge progress has been made in research of polymer based synthetic mimics of antimicrobial peptides (SMAMPS). Much work on this topic using ROMP as the polymerization technique was done by Tew et al. who established a “molecular construction kit” for ROMP derived SMAMPS (see Fig. 17) [190–194]. Exemplary polymers are shown in Fig. 17. The polymers were evaluated regarding their antimicrobial performance by systematically altering (i) the hydrophobic moieties, (ii) the overall charge and (iii) the molecular weight. With the tests two characteristic values were determined. The minimum inhibitory concentration (MIC_{90}) is the polymer concentration in solution that inhibits 90% of bacterial growth and the hemolytic activity (HC_{50}) which is the value at which 50% of mammalian red blood cells are lysed up in exposure to the synthetic polymer [190]. High hydrophobicity leads to high toxicity for both, pathogens and mammalian cells. Moreover solubility issues become a problem. Regarding the charge density, a certain threshold has to be exceeded to maintain biocide activity. Additional charges do not improve the performance [195]. As for the molecular weight of homopolymers, too high values prevent biocidic activity.

9. Olefin metathesis on bio-based resources

Regarding the current situation of ongoing depletion of fossil resources and the permanent increase of green house gases in combination with a growing need for high-tech “plastics”, it is only logical to implement the principle of green chemistry in polymer science. Plant oils, featuring multiple unsaturated carbohydrate chains, offer a broad field for metathesis chemistry. Plant oil-derived fatty acids and their derivatives are of special interest in polymer chemistry as they display high potential to replace or at least rival petrochemical polymers. The latest developments on this sector have been recently summarized in a review by Michael Meier [196]. Some highlights making use of olefin metathesis will be presented in the following.

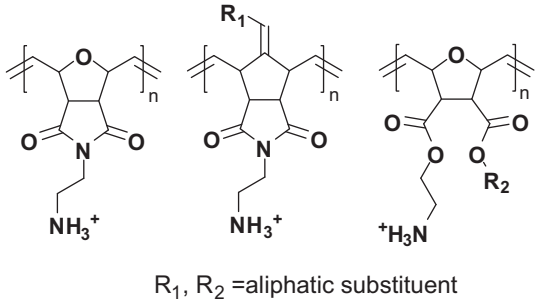
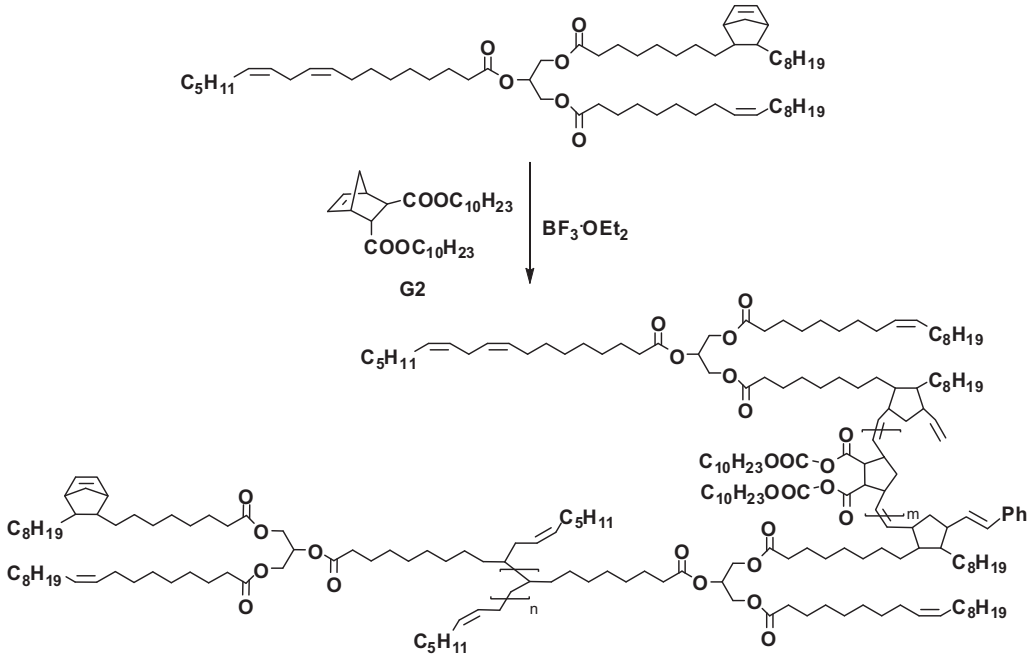


Fig. 17. ROM polymers for SMAMPs [190].



Scheme 8. Dilulin™ copolymerized and crosslinked with a norbornene derivative using ROMP and cationic polymerization to obtain a bio-based rubber with exceptional mechanical properties [206].

Different numbers and positions of the double bonds as well as functional groups within the fatty acids chain provide a pool of interesting starting materials for metathesis based transformations. Cross-metathesis of fatty acid esters or fatty alcohols with acrylates yields long chained diesters or ω-hydroxy-fatty acids for the synthesis of polyesters and polyamides [197–199].

ADMET was used to polymerize a monomer made from renewable resources. The use of chain stoppers allowed for controlling the molecular weights and for obtaining telechelic polymers [200], or hyperbranched species [201]. Very recently, Meier reported on the synthesis of castor oil fatty-acid derived polyesters suitable for flame-retardants due to a phosphorous containing monomer. To control the content of flame retardant, the corresponding monomer was copolymerized with a long chain α,ω-divinylester (undecyl-undecanoate) and endcapped with 10-undecanoate by means of ADMET bulk polymerization with **G2** [202].

Plant oil-derived monomers have also been used for the synthesis of cross-linked polymer networks for thermosets or composite materials. In this matter, the commercially available Dilulin™, a norbornenyl modified linseed oil, plays a central role [203]. Upon addition of cross-linkers like DCPD-similar derivatives, thermoset resins are obtained that are suitable for e.g. glass fibre composite materials with favourable mechanical properties [204].

Other norbornene functionalized plant oils used for thermosets are castor oil or soybean oil. Depending on the corresponding side chain features thermosets exhibiting different thermal and mechanical properties were obtained. They were comparable to petroleum based materials (HDPE) [205]. A bio-based rubber with exceptional material properties was synthesized by a combination of ROMP with cationic polymerization in a Dilulin™ norbornene diester (NBDC) system (see Scheme 8) [206]. The implemented NBDC ROM polymer causes drop of the glass transition temperature from 8.6 °C (no NDBC) to −17.4 °C (30%wt. NBDC), which is highly desirable for rubber materials. This is due to a lower rate of possible crosslinking. Also the tensile tests prove a large improvement in mechanical behaviour (reduction of brittleness) due to NBDC implementation: 52% elongation at break (30%wt. NBDC) compared to 17.6% (no NDBC). In other reports, which should be mentioned it is made use of naturally occurring macrocyclic bile acids as shape-memory polymers, which were prepared by entropy-driven ROMP [207–210]. Other macrocyclic natural products bearing ED-ROMP able double bonds comprise Sophorolipids [211,212].

10. Liquid crystal polymers

Liquid crystal polymers (LCP) represent a special group within self-assembling materials. They are intensively investigated in the context of nonlinear optics, electronics or biomedical matters. The organisation within the polymer is responsive to an external trigger that can be heat, light, magnetic or electrical fields [213–215]. A review on LCPs derived from metathesis polymerization methods was published by Trimmel et al. in 2005 [216]. The following chapter highlights some recent works on that many-sided topic.

Within LCPs, elastomers or gels are of special interest because they combine the elasticity of the rubber part and the anisotropic behaviour of the side chain mesogen in an amorphous cross-linked network. The macroscopic properties of the final material are determined by the flexibility and microstructure of the polymer backbone, degree of cross-linkage, choice and frequency of the mesogen and spacer length [213]. With conventional techniques like radical polymerization in presence of a crosslinker [217–219] or random crosslinking of hydrosiloxane based polymers [220,221] all these parameters are hard to control. The use of well defined ABA-triblock copolymers was a crucial step to better control over the macromolecular structure [222]. Terentjev et al. used terphenyl based “A-blocks” that led to a well phase-separated system where the nematic order of the mesogen goes hand in hand with telechelic cross-linked A-blocks, leading to a perfect shape-memory system [222]. In 2006, Schrock et al. published the successful synthesis of several side chain liquid crystal polymers (SCLC) on ABA-triblock basis by means of ROMP, using a bimetallic Mo-based initiator [223]. The monomers were two different norbornene derivatives featuring a nematic and a smectic mesogen.

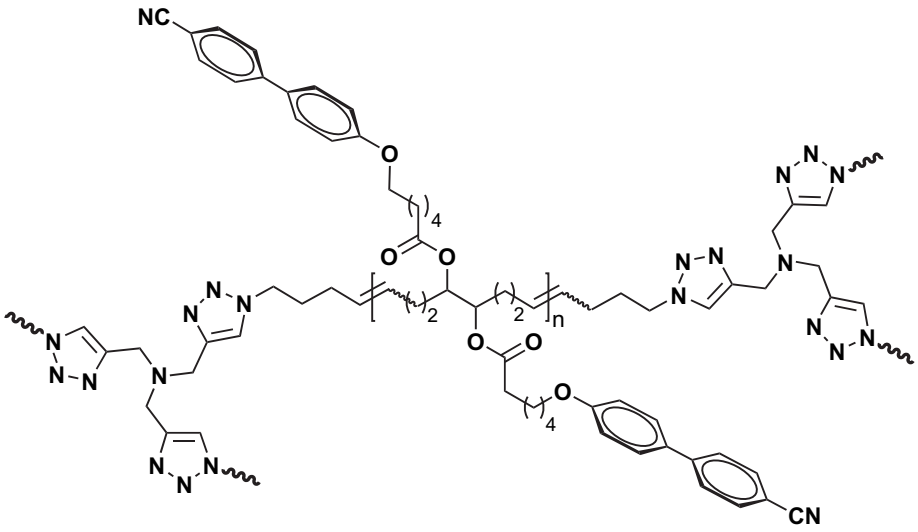


Fig. 18. Architecture of a "click"-crosslinked SCLC polymer [214].

Alkyl chains as well as polyethylene oxide chains were established as variable spacers between the backbone and the mesogen moieties. The amorphous outer blocks were made of the commonly used crosslinker methyltetracyclododecene. More recently, Grubbs and Kornfield combined ROMP and "click"-chemistry to assemble perfectly defined SCLC polymers [214]. One or two cyano-biphenyl mesogenic groups were attached to the cyclooctene monomers with a short alkyl spacer, leading to a very flexible alkyl-chain backbone, which is favourable for fast segmental dynamics in the final application. In order to gain control over the network consistency, crosslinking was done via a telechelic CTA (chain transfer agent) to obtain primary bromides. After polymerization they were reacted into azides to give a "click-couple" with tripropargylamine (Fig. 18).

Variation of the mesogen itself, but also tuning the way of anchoring at the backbone can have influence on the type of mesophase. Due to their handedness, cholesterols are known to form chiral nematic phases. Depending on the type of the backbone, additional functional groups and spacer length, the mesophase can also be turned into smectic structures. Cholesterol based LCs have proven immense usability in optoelectronics and colour information technology (LCD displays, optic stimuli responsiveness). Also for biomedical applications they are of great value due to their excellent biocompatibility and suitable mechanical properties [224,225]. Tissue engineering or artificial muscles (actuators) are just two catch phrases that give an idea about the medical relevance of well defined systems in this context. Very recently, Kasi et al. published SCLC with cholesterol mesogens prepared with ROMP establishing a smectic mesophase, presumably due to the enlarged rigidity of the norbornene backbone [226].

Mesogens that are attached laterally, generally exhibit a higher degree of symmetry than terminal attached mesogens. On the other hand, these LCPs usually lead to "only nematic" mesophases because of sterical constraints. A way to circumvent this problem is to terminate the mesogenic substituents with immiscible fluorocarbon or siloxane segments that force the construction into smectic layers [216]. Using ROMP for the definite construction of LCPs is highly effective and convenient. Still, the possibility to obtain main chain liquid crystal polymers (MCLCP) is not provided. In contrast, ADMET [83] and ALTMET [124] polymerization techniques can produce MCLCPs [216,227,228]. Walba et al. reported on MCLCPs that can undergo specific smectic phase transitions when exposed to an electric field [229]. A difunctional monomer exhibiting a dimethylvinylsilyl group at one end and a terminal olefin on the other terminus was polymerized with **H2** in CH_2Cl_2 under reflux conditions for 3 days and yielded oligomers with about 20 repeating groups (*cf.* Fig. 19).

11. Porous ROM polymers and SI-ROMP

Highly porous materials have been subject of intensive research during the last years. These materials combine properties such as good mechanical strength, insulation features, potential for separation methods like chromatography etc [230]. According to literature three various ways to obtain highly porous materials prepared via ROMP are known: (i) concentrated emulsions (ii) phase separation and (iii) secondary processes.

(i) The preparation of highly porous polymeric materials via concentrated emulsions leads to so called poly(HIPE)s. For this purpose high internal phase emulsions (HIPEs) are used as templates. HIPEs already have long industrial tradition in food preparation, fuel- oil- and cosmetic-sector [231]. The fabrication of poly(HIPE)s is a simple process in which an emulsion containing a continuous and a droplet phase is formed and one of the phases is cured in some manner. The respective monomer, plus a crosslinker and an adequate surfactant are mixed together, the droplet phase is added slowly and the whole mixture is stirred constantly to receive the desired

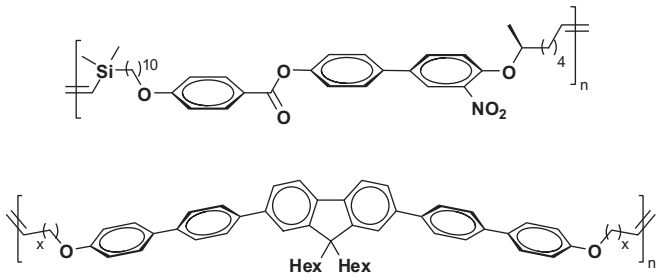


Fig. 19. Exemplary MCLCPs prepared using ADMET taken from Ref. [229] (above) and Ref. [228] (below).

emulsion. The resulting HIPE is then cured. In principle poly (HIPE) materials are characterized by an internal void volume exceeding 80%, by tuneable cell diameters and by interconnecting windows between the individual pores [231].

The implementation of ROMP as the curing procedure was first introduced by Deleuze in 2002 [232]. Even if the application of ROMP turned out promising for poly(HIPE)s, not many further investigations were done. Advantages of ROMP compared to the radical polymerization techniques, include the possible cure at room temperature or even at lower temperatures avoiding degradation of the emulsion during polymerization. Moreover the possibility of functionalization of the double bonds after the curing process is dramatically widening the range of potential applications [233]. The living character of ROMP permits grafting of a second polymer onto the poly(HIPE) structure or attaching a functional group for instance by the use of terminating agents [234]. By now, three different norbornene based monomers for the preparation of porous foams have been tested: tetracyclo [6,2,1^{3,6},0^{2,7}] dodeca-4,9-diene (BVD), tetracyclo[6,2,1dicyclopentadiene (DCPD) and tetracyclodecen (DMON). **G1** was used for all three monomers. The results gained using BVD were auspicious. A porous structure with a pore diameter of 15 μm and a window diameter around 4 μm was obtained [232]. In contrast, with DMON a microcellular foam was generated, but pores exhibited a large size distribution and low pore connectivity. Poly (HIPE)s prepared with DCPD didn't even reveal the presence of pores. This result could be explained by an unstable emulsion where the water droplets of the droplet phase coalesced and the emulsion segregated [233].

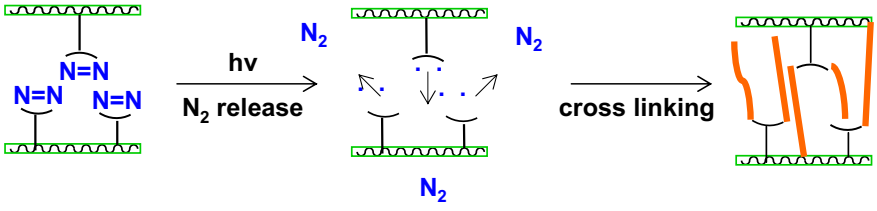
(ii) An extensive research on porous polymeric materials via phase separation was done for their application in monolithic separation materials [235]. Nowadays monolithic materials have emerged as powerful and widely used chromatographic tool for several chromatographic applications. At the beginning, the majority of monolithic media based on organic polymers were prepared via radical polymerization using methacrylates or styrene-*co*-divinylbenzene as monomers. By now, besides the preliminarily mentioned radical polymerization technique, a series of alternative methods were established e.g. polymerization via UV- or γ-irradiation, polycondensation, polyaddition [236], electron beam irradiation [237,238] and ROMP. The latter has emerged as the most outstanding one because of the broad range of monomers applicable, the high potential for functionalization and its good reproducibility. The combination of ROMP with grafting and precipitation techniques gives rise to manifold ways of functionalization [239].

Monolithic separation media synthesized by ROMP are used for simple columns for the separation of biomolecules via a reversed phase mechanism [239], columns for High Performance Liquid Chromatography (HPLC) [240] and capillary HPLC [235], or the synthesis of norbornene-based weak cation exchange capillary columns [241]. Apart from conventional columns, monolithic media were also utilized for the production of membranes for solid phase extraction [242]. Beside these separation applications, research on monolithic materials for biodegradable scaffolds for osseous- and soft tissue engineering [243] and for copolymer scaffolds was made [244].

The synthesis of monolithic material via ROM polymerization affords a monomer, a crosslinker, an initiator and a porogenic solvent for phase separation to form the desired porous microstructure. In general non substituted NBE as monomer and 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo,endo*-dimethanonnaphtalene (DMN-H6) as crosslinker in the presence of a mixture of 2-propanol with toluene as the porogenic solvent, are used. **G1** initiates the so called "in-column" polymerization. The resulting materials display excellent separation performance and good stability at ambient temperatures. Still they are prone to oxidation at the tertiary allylic carbon, resulting in aging of the material and in a long-term stability of less than 1000 injections. Another system described in literature is *cis*-cyclooctene as monomer, tris(cyclooct-4-enyl-1-oxy)methylsilane as crosslinker and the same porogen as used for the NBE system [245]. Due to the lower ring strain of the cyclooctene, the more reactive **G3** was used as the initiator of choice. Like expected the long-term stability of the newly invented system was improved and after 1000 injections, the separation performance remained unchanged [246].

(iii) While in the aforementioned strategies polymerization and formation of the pores happen in situ, some approaches have been done where the porous structure is developed in a second step. Aerogels prepared from ROM polymers are rather unexplored. Generally aerogels are prepared by removing the solvent contained in a gel matrix using a drying process, namely supercritical-, freeze- and ambient-pressure drying have been explored [247]. Recently Gould et al. published a strategy to use ROMP for the preparation of new insulation materials. DCPD was used as the monomer. The DCPD solution turned to an opaque gel during polymerization. Supercritical drying with CO_2 was used to extract the solvent from the gel and to form the desired nanoporous structure. The polydicyclopentadiene aerogels demonstrated high porosity, low thermal conductivity values and inherent hydrophobicity [248]. Instead of DCPD, Weck et al. used cross-linkable poly(lactic acid)-*block*-poly (NBE). The copolymer was dissolved in an appropriate solvent and cooled down below its freezing point. The frozen solvent was then evaporated by freeze-drying under reduced pressure. Variations of cooling temperature, polymer concentration and solvent led to different pore sizes between 50 and >300 μm. The best mechanical stability was gained with a pore size between 150 and 300 μm [244].

Another totally different approach is the formation of pores via a photocuring process. For this purpose a norbornene derivative bearing a light sensitive diazene bridge was synthesized and polymerized before being photo cross-linked. During this photocuring process nitrogen gas is released yielding pores crosslinking of the polymer chains occurs (see Scheme 9) [249].



Scheme 9. Photocuring process for the synthesis of porous materials. Redrawn from Ref. [249].

Another application is the functionalization of surfaces which is used for tailoring properties such as surface energy and friction. Surface-initiated ROMP (SI-ROMP) was used to attach alkylated [250] and fluorinated [251] polynorbornene chains to a gold surface in order to achieve films of tuneable thickness in the range of 20 nm to several μm (Fig. 20). Earlier work of this group investigated ionomer films on Pt-modified gold electrodes [252].

Another example comprises the formation of diblock-copolymer brushes on gold substrates, following the demand for multiple surface properties [253]. Furthermore, SI-ROMP on silicon was performed. Bare silicon was modified by chemomechanical treatment (scribing) with α,ω-diolefins followed by growing norbornene strands from the surface. This modification resists the electroless deposition of copper enabling for the structured deposition of the latter [254]. Furthermore, anodization lithography was used to prepare nanopatterned polymer brushes on silcon [255]. Also nanoparticles have been functionalized by SI-ROMP [256]. A feature article on olefin metathesis on nanostructures covers further work which is not mentioned here [257].

12. ROMP for self-healing materials

All previous chapters mainly dealt with the modification of micro- and macrostructure of ROM polymers. In the following another outstanding feature of metathesis polymerization is highlighted using the example of intelligent materials. Polymers and composite materials are used in a wide range of applications including vehicles, electronics, biomaterials and many more. Due to their utilization in "real life" these materials are exposed to many impacts that can cause damage e.g. UV-irradiation, heat, pressure, chemicals and so forth. These forces cause, besides visible and easily detectable defaults, also hardly visible or even invisible microcracks in the polymer matrix. As a consequence a reduction in fibre-dominated properties such as tensile strength and other material fatigues occur [258]. If these microcracks coalesce in structural composites, delamination and fibre fracture follows.

The concept of self-healing polymers was first proposed in the early 1980s [259]. Since then many different methods for self-healing polymeric materials have been published. Regarding thermoplastics and thermosets many diverse methods to implement the healing sequence have been tested. Regarding thermoplastics, procedures like molecular interdiffusion, photo-induced healing, recombination of chain ends, self healing via reversible bond formation, or self-healing by nanoparticles, were established [258]. Since thermoplastics and thermosets exhibit totally diverging features, the development of self-healing concepts for thermosets has followed a different route. The majority of these approaches involve the incorporation of the self healing agent into the polymeric matrix. Some selected examples are the Hollow Fibre Approach, microencapsulation using ROMP, the utilization of thermally reversibly cross-linked polymers, chain rearrangement etc [258].

The first use of ROMP for self-healing materials was introduced by White et al. [260]. Healing is accomplished by the release of microencapsulated healing agent (ROMP monomer) from a urea-formaldehyde shell (*cf.* Fig. 21) [261]. The corresponding ROMP initiator is embedded in the material matrix. If a microcrack occurs, the microcapsules rupture, the healing agent convenes with the initiator and polymerizes. Thus, the crack gets filled up, the crack faces are bonded and further crack growth is prevented. For a successful healing procedure the agents have to remain inert during the manufacturing process and the entire material's lifetime.

The first described and since then most established self-healing system is made up of *endo*-dicyclopentadien (DCPD) as the healing agent and a **G1** as the polymerization trigger, incorporated in an epoxy matrix. This system works well but high catalyst loadings (2.5 wt.%) are inevitable due to low dispersion of the complex in the epoxy matrix and due to catalyst deactivation upon exposure to the amine curing agent diethylenetriamine (DETA) contained in the epoxy matrix. Recently Rule et al. published an alternative to prevent/diminish the deactivation of the initiator by incorporating it into paraffin wax. Upon fracture, the released DCPD dissolves the wax microsphere and polymerization can occur. They also suggest that the wax microglobules lead to a better dispersion of the initiator particles in the epoxy matrix. Studies about the effect of wax on self-healing revealed the maximum average healing efficiency being achieved at 0.75 wt.% catalyst loading [262]. This significant decrease of initiator loading lowers the overall costs of these self-healing systems. It is absolutely essential, that the

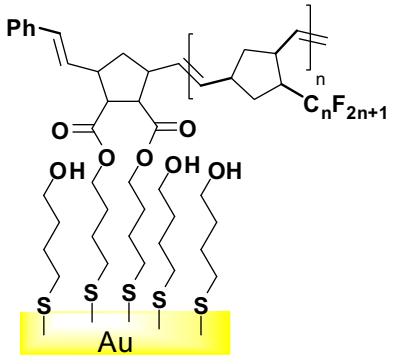


Fig. 20. Surface-initiated ROMP with fluorinated norbornene monomers.

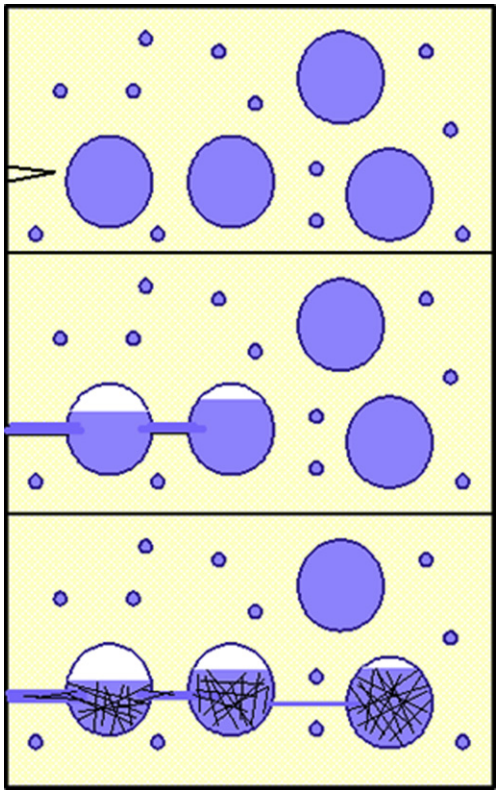


Fig. 21. Concept of automatic healing using encapsulated healing agents and ROMP initiators. Redrawn according to Ref. [261].

healing process can take place at room temperature or lower, and that the viscosity of the agent is low enough to fill up the cracks completely before polymerization occurs. Moreover, thermo-mechanical properties and adhesive strength of the polymer formed has to match the matrix [263]. DCPD features some of the mentioned properties such as high toughness and strength achieved by the cross-linked structure of poly(dicyclopentadiene). Still, DCPD shows a slow *in-situ* polymerization rate and is not capable for low temperature applications due to its melting point of 33 °C. Recently some approaches to by-pass these problems were propound. The group around Moore et al. suggested the use of *exo*-DCPD instead of the *endo* derivative. The *exo* stereoisomer exhibits a much faster polymerization kinetic leading to reduced gelation times. Regrettably this monomer is not capable of dissolving the wax which leads to lower healing efficiencies compared to the *endo*-DCPD system [264]. Another approach is the utilization of 5-ethylidene-2-norbornene (ENB) as healing agent. This monomer combines high polymerization activity and a low melting point at −80 °C. However, in contrast to the DCPD, ENB forms a none-cross-linked polymer which possesses inferior mechanical properties. Hence, a mixture of ENB with a norbornene-based crosslinker was used [263]. This monomer mixture still features a low viscosity comparable to the original ENB and exhibits a reduced gelation time, resulting in low initiator loadings.

As for the shell thickness of the microcapsules, the wall size should be thick enough to survive handling and manufacturing of the material and thin enough to rupture when microcracks occur. The group of Brown and co-workers suggested that a shell thickness ranging from 160 to 220 nm fulfils these requirements [265]. Also the amount and the diameter of the microcapsules have to be considered since they affect the viscosity of the resin and alter the toughness of the matrix. Self healing efficiency tests have been performed by tensile, fracture and fatigue tests in neat epoxy matrices and in fibre reinforced composites [266].

Over the past years many new approaches and techniques for self-healing materials were investigated and already established concepts were upgraded. In future the focus will be set on the commercialisation of self-healing materials and on the investigation of biological healing mechanism for synthetic material.

13. Conclusion

This review should give an insight into the latest developments in metathesis polymerization chemistry, focussing on ROMP. It illustrates the immensely growing scope of possible uses of ROMP in various fields of chemistry, including biocidic polymers, organo-electronics or smart materials like self-healing composites. Generally, ROMP is amongst the polymerization techniques of choice whenever polymers exhibiting tailored features are required. Existing catalysts show special tolerance towards moisture, oxygen and numerous functional groups. Mostly, mild reaction conditions are sufficient and no co-reactants are necessary for successful polymerizations. Combination of ROMP with other synthetic polymerization techniques such as RAFT, ATRP, or click-chemistry opens even more ways for novel synthetic routes. Besides high-tech polymers with targeted properties, ROMP is also suitable for the synthesis of elastomers, thermoplastics or thermosets from easily available resources e.g. fatty acids from natural oils or DCPD, which is a by-product in petrochemical industry. However, there are some severe drawbacks that still impede ROMP from being extensively employed in industry. Restrictions are given by a limited contingent of polymerizable groups which allow for living polymerization. Functionalities like primary or secondary amines still cause problems due to initiator deactivation, affording in most cases additional protection and deprotection steps. As for the initiators, the high costs for the ruthenium complexes and the potential toxicity of remains in the polymer display a serious confinement. With the development of PA-ROMP a ground-breaking way to circumvent these problems has been introduced. Another challenge for the future is to achieve better control over the microstructure of the polymers, a task which might be solved by disclosing novel initiators. Anyway, researchers should keep in mind that the key features of state of the art initiators **G3** or **M31** (fast and complete initiation, controlled living polymerization) are not to be lost in those novel initiators. Although there is much to be expected in this research area, olefin metathesis has already proven more and more often to be a valuable tool when it comes to precision in macromolecular chemistry. In short, ROMP is a privileged polymerization technique, it is fast, functional group tolerant, reliable, flexible and versatile. Use it!

Acknowledgments

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