Block Copolymers via ROMP – Awakening the Sleeping Beauty

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Summary: This paper on recent developments in block copolymerisation using ring-opening metathesis polymerisation summarizes about 60 publications and discusses current trends.

Keywords: block copolymers; phase separation; ring-opening metathesis polymerisation; self assembly

Introduction

Block copolymers have attracted attention as they have been recognized as materials that not only combine properties of different polymers in one material but can also lead to materials with even totally new characteristics [1]. In 1985 ring-opening metathesis polymerisation (ROMP) [2] was used to synthesise block copolymers for the first time [3]. Intensive research work brought up many publications on block copolymers each year; however block copolymers made by ROMP hold only a small partition of this topic (c.f. Fig. 1). The reasons can be found at the initiator's side. In principle they are well suited for the purpose of block copolymer preparation because in many cases living polymerisation is provided. Nevertheless even more recent ROMP initiators show some disadvantages. Ruthenium complexes most prominently represented by $(PCy_3)_2(Cl)_2Ru{=}CHPh$, the 1st generation Grubbs initiator (**1**) and $(H_2IMes)(PCy_3)_2(Cl)_2Ru{=}CHPh$ (H_2IMes = N,N-dimesityl-4,5-dihydroimidazol-2-ylidene) (**2**) the 2nd generation Grubbs catalyst are hampered due to a low activity in case of **1** and low initiation efficiency in case of **2**. Both disadvantages can be tackled by using Schrock-type initiators (**3**, **4**) which are very active and provide complete initiation in most cases. The main drawback of **3** and **4** is their incompatibility with protic functional groups and even more important moisture and oxygen such that their practical applicability is restricted [4].

In the following sections the preparation of block copolymers using these different initiators is described grouped by their possible application intended. Emphasis is given on the recent

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years, which are not covered by the review of Buchmeiser [4] and on the latest developments in initiator design, which will in all probability boost the field of block copolymers prepared by ROMP in future.

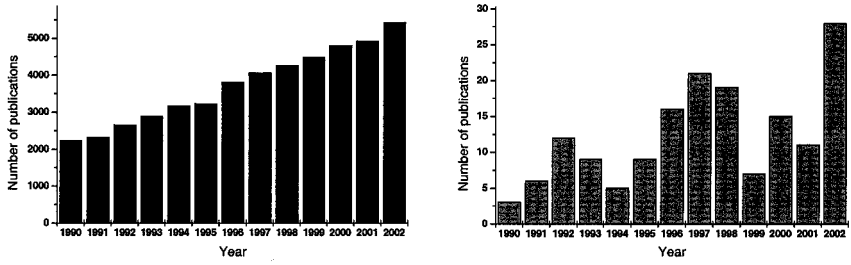


Figure 1: Number of block copolymer publications per year (left); block copolymer publications per year synthesised via ROMP (right)

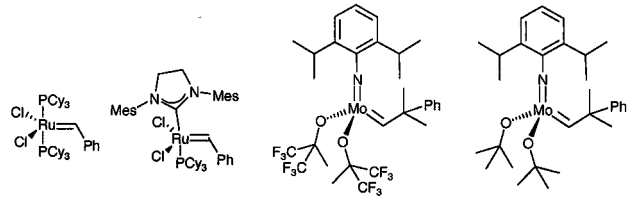


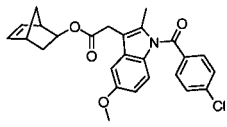
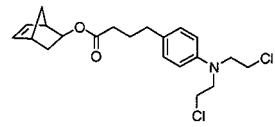
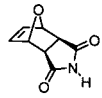
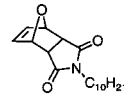
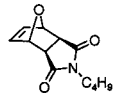
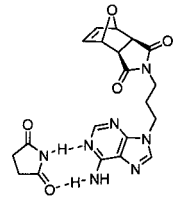
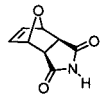
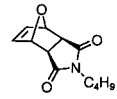
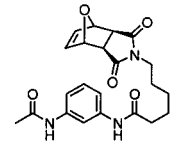
Figure 2: Grubbs – (**1**, **2**) and Schrock – (**3**, **4**) type initiators

Biologically relevant block copolymers

During the last decade research of functionalised polymers for biological and medicinal applications has seen considerable growth. Notably when used as scaffolds for drug delivery [5] the polymer materials offer several advantages over their monomeric precursors, including longer retention time in the body, lower toxicity, and a greater specificity of action. Since most therapeutic strategies rely on a combination of multiple drugs to achieve an optimum benefit [6], well-defined block copolymers which are functionalised with a high density of different drugs may be an extremely useful method of drug delivery. A narrow polydispersity can be advantageous for the dosage control in pharmacotherapy and pharmacokinetics. Watson et al. reported on the utilization of living ROMP for the preparation of such materials [7]. Commercially available compounds with demonstrated anticancer activity were targeted for modification with *exo*-5-norbornen-2-ol. The block copolymer synthesis was done with the Grubbs catalyst of the 1st generation (**1**) (Table 1: entry 1) resulting in a block copolymer with

a M_n of 27600 and a PDI of 1.20.

Table 1: Block copolymers with different monomers

Entry	Initiator	Monomer 1	Monomer 2	Monomer 3	PDI
1[7]	1				1.20
2[8]	1				1.09
3[11]	2				1.20 – 1.60
4[16]	1				1.08 – 1.14

Dalphond et al. published the synthesis of block copolymers of *exo*-7-oxabicyclo[2.2.1]hept-5-en-2,3-dicarboximide [8]. The carboximide units have been previously shown to exhibit biological activity [9], can selectively bind to the nucleic acid base adenine by hydrogen bonding [10], and are readily functionalizable by deprotonation, followed by nucleophilic substitution. This functionalization was demonstrated with a long alkyl chain and the observed molecule was used as comonomer for the synthesis of the block copolymers (Table 1: entry 2). Initiator **1** was chosen to obtain a block copolymer with a PDI of 1.09. The self-assembly of these block copolymer leads to the formation of nanoscale micellar aggregates with surface localization of the molecular recognition dicarboximide units.

Another example for a potential biomolecule sensor and DNA-delivery agent was shown by Bazzi et al. [11]. They reported the synthesis of adenine containing block copolymers by modification of 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide with adenine and the ability of these hydrogen-bonding and self-complementary block copolymers to self assemble into nanoscale rod morphologies. A polymerisation with **1** was not possible due to the

coordination of the adenine moiety to the initiator. **2** generated a homo polymer in 70 % yield. Higher monomer conversions could not be achieved, due to the insolubility of the polymer, which possesses self-complementary adenine units. Addition of succinimide as complementary molecule to protect the monomer via hydrogen bonding significantly increased the yield to 90 % as well as the solubility of the polymer. Using this noncovalent protecting method and employing **2**, block copolymers of the adenine containing monomer with *exo-N*-butyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (Table 1: entry 3) with PDIs between 1.20 and 1.60 were obtained.

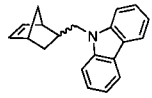
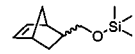
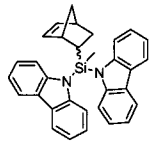
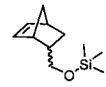
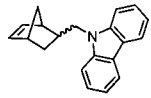
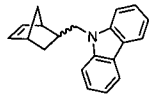
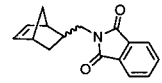
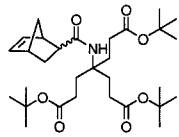
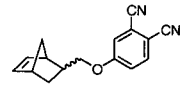
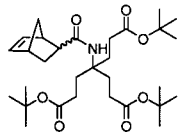
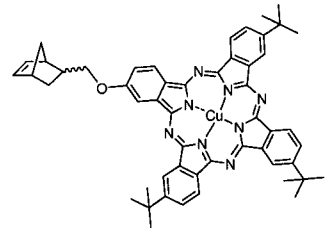
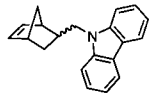
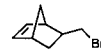
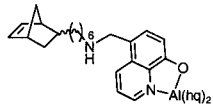
Also the selective recognition potential of DNA itself was used for the development of new detection strategies [12], novel nanostructures [13] and the construction of nanoelectronic structures [14]. Watson et al. demonstrated that post-polymerisation modification of ROMP block copolymers with DNA can lead to DNA/polymer hybrid materials with a number of interesting properties associated with the hybrid structure [15].

The preparation of self-complementary ABC triblock copolymers using initiator **1** with polydispersity indices between 1.08 and 1.14 was published very recently (Table 1: entry 4) [16].

Block copolymers for electrical and electrooptical applications

Carbazolyl-substituted polymers are well known as precursors for electrophotographical materials with valuable optical and photoconductive properties [17]. Notably the group of Liaw has done intensive work regarding the ROMP of carbazole-functionalized norbornene derivatives over the recent years. One article describes the synthesis of block copolymers of carbazolyl-substituted norbornene and a trimethylsilyl-protected alcohol-functionalised norbornene derivative. Several studies have reported that microphase-separated block copolymers with hydroxyl functional groups are useful templates in the synthesis of semiconducting metal sulfide nanoclusters [18].

Table 2: Block copolymers with different monomers

Entry	Initiator	Monomer 1	Monomer 2	PDI
1[18]	1			1.25
2[19]	1			1.22
3[20]	1			1.10 – 1.47
4[21]	1			1.4
5[24]	1			1.9
6[24]	1			1.9
8[30]	1			-
9[31]	2			1.53 – 1.74

A combination with carbazole functionalised norbornenes in block copolymers (Table 2: entry 1) is expected to exhibit novel optoelectronic properties. The polymerisation was carried out with initiator **1** and the obtained block copolymer had a PDI of 1.25. Microphase separation observed by TEM displayed a strong binding of cadmium into the alcohol domain.

Another work about ROMP block copolymers functionalized with charge-transporting carbazole groups and domains suitable for the in situ synthesis of CdS nanoclusters was published recently (Table 2: entry 2) [19]. The direct polymerisation of the unprotected alcohol functionalised norbornene derivative was reported to be impossible using of initiator **1**.

Additional work by Liaw et al. showed the synthesis of block copolymers of 5-(*N*-carbazolyl methyl)bicyclo[2.2.1]hept-2-ene (CbzNb) with 1,5-cyclooctadiene using initiator **1** (Table 2: entry 3) yielding polymers with PDIs between 1.10 and 1.47 [20].

Furthermore, block copolymers of CbzNb with 5-(phthalimide methyl)bicyclo[2.2.1]hept-2-ene (NbMPI) were synthesised (Table 2: entry 4) [21]. The PDI of the polymers depended on the order of monomer addition. Using CbzNb as the first monomer resulted in a polymer with a PDI of 1.4. By changing the order of monomer addition, a polymer with a PDI of 1.7 was obtained. The incorporation of the phathalimide group remarkably enhanced the thermal stability of the polymer.

Roh et al. reported the synthesis of diblock polymers containing two of three moieties essential for the photorefractive effect in discrete blocks within the same polymeric material (Figure 3) [22]. As potential charge transport block served 9-(3-methyl bicyclo[2.2.1]hept-5-ene-2-ylmethyl)-9H-carbazole. To introduce the non-linear optic property, the 3-position of 9-(3-methyl bicyclo[2.2.1]hept-5-ene-2-ylmethyl)-9H-carbazole was brominated with *N*-bromosuccinimide. After the formation of the block copolymer with initiator **1** the bromo-functionality was converted to a 2,2-dicyanovinyl group.

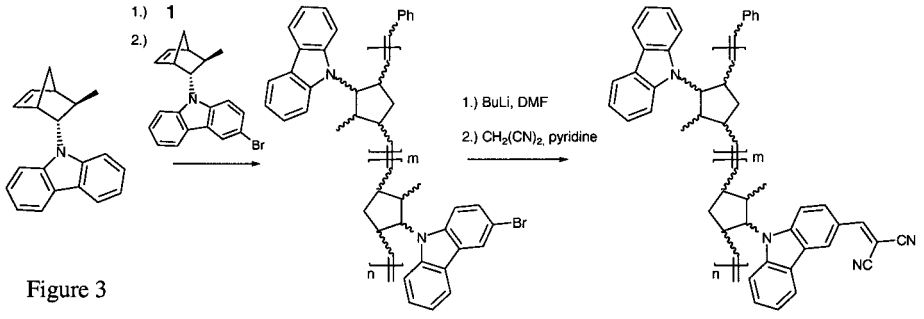


Figure 3

The obtained block copolymers showed PDIs ranging from 1.5 for the brominated block copolymer to 3.0 for the cyanovinylated copolymer.

Bazzi et al. synthesised conjugated polymer precursors via ROMP of dichlorocarbonate-substituted norbornene derivatives (Figure 4) [23]. Derived block copolymers with 4-Decyl-

10-oxa-4-aza-tricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione are able to self-assemble in solvents to form spherical micelles. Moreover they report that hydrolysis of the precursor polymers had resulted in the generation of a new class of low-band gap conjugated block copolymers. Additionally it was possible to modify the 1,2-diol-groups of the resulting conjugated polymer with functionalities like chromophores, metals or luminescent moieties. Polydispersities were of about 1.4.

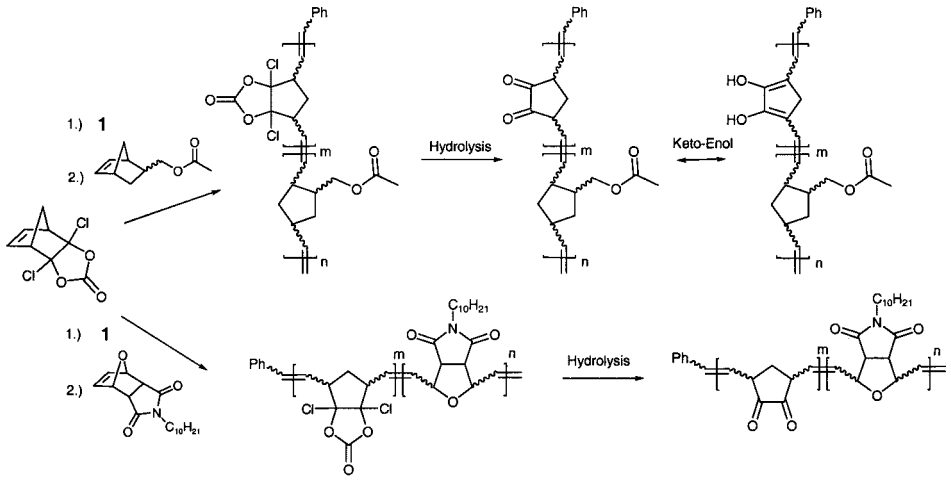


Figure 4

Kimura et al. reported the synthesis of amphiphilic poly(norbornene) block copolymers from monomers bearing a copper phthalocyanine and a branched hydrophilic side chain using initiator **1** (Table 2: entries 5 and 6) [24]. These materials are expected to open new possibilities for the design of functional nanostructured materials for the construction of molecular photonic and electronic devices. Further they described the direct polymerization of a phthalonitrile containing norbornene derivative with initiator **1** to generate block copolymers. Kimura et al. obtained block copolymers with PDIs of about 1.9. Investigations of the aggregation behaviour showed that the phthalocyanine block copolymer forms spherical micelles in alkaline aqueous solution. Referring to the literature a polymerisation of cyano-groups containing norbornenes with initiator **1** should not be feasible [25,26].

Another possible application approached in which block copolymers for objective analysis of odors as well as for the intellectual challenge of mimicking the mammalian sense of olfaction in "electronic noses" [27]. Numerous implementations of artificial noses have emerged;

however, the most prevalent devices are based on detecting a physical or chemical change in a polymer film upon exposure to a gaseous analyte [28]. Matzger et al. investigated the potential of ROMP block copolymers in carbon black/polymer composites for such applications [29].
Liaw et al. synthesised a ROMP diblock copolymer, with one segment containing carbazole moieties and the other segment bearing methylbromide-groups, which was used as initiator to mediate ATRP of methyl methacrylate (Table 2: entry 8) [30].
Recently Meyers et al. published the syntheses of ROMP block copolymers containing aluminium tris(hq) (hq = 8-hydroxychinoline), a very stable and fluorescent solid-state material, which is interesting for the application in OLEDs (Table 2: entry 9) [31]. Other investigations cover the possible applications of ROMP block copolymers as polymer electrolytes in batteries [32].

Liquid crystalline block copolymers

Li et al. reported the synthesis of liquid crystalline block copolymers as model systems for "artificial muscles" [33]. They synthesized a side-on LC/Iso diblock copolymer by first polymerizing the LC block using ROMP with initiator **1** and then the Iso block using ATRP (Figure 5), resulting in polymers with PDIs around 1.3. An important structural characteristic of these microphase segregated systems was a significant decrease of the lamella spacing from the glassy or crystal to isotropic phase after a continuous shrinking over the nematic range and a steep decrease at the nematic-isotropic transition.
Another example of a side chain liquid crystalline polymer was reported by Viertler et al. [34]. They combined a smectic liquid crystalline block with a partial crystalline unpolar block using the Schrock-type initiator **3**. The obtained block copolymers showed PDIs between 1.2 and 1.3 and lamellar microphase separation.

Combination of ROMP with other living polymerization methods

"Living" polymerisation, such as ROMP, ATRP (atom-transfer radical polymerization), GTP (group transfer polymerization) and anionic polymerization enable the synthesis of well defined block copolymers with narrow molecular weight distributions. However, the set of monomers is limited for each polymerisation method. The combination of two different polymerization methods enables one to circumvent this limitation [35].

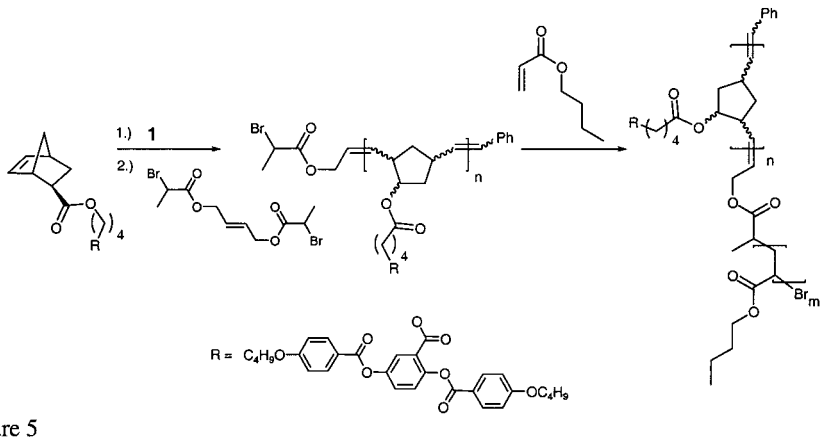


Figure 5

Notestein et al. synthesized ROMP-anionic block copolymers by terminating a ROM polymerisation with a polymeric aldehyde which was obtained via anionic polymerisation based on a Wittig-like coupling (Figure 6) [36]. This procedure however, required a subsequent fractionation, to isolate the pure diblock copolymers with published polydispersities between 1.03 and 1.08.

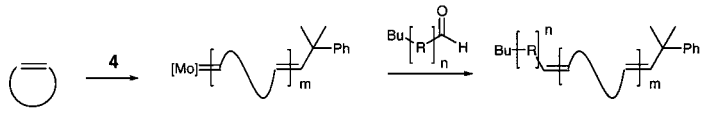


Figure 6

The syntheses of poly(norbornene)-*b*-poly(styrene) block copolymers via combination of ROMP with a radical polymerisation mechanism were reported by Miura et al. (Figure 7) [37]. The obtained block copolymers showed rather moderate PDIs around 2.0.

Bielawski et al. published the synthesis of an initiator (**6**) that enables the mediation of ROMP and ATRP polymerisation simultaneously (Figure 8) [38]. They produced poly(cyclooctadiene)-*b*-poly(methyl methacrylate) block copolymers in a "one pot" copolymerisation with PDIs of 1.6.

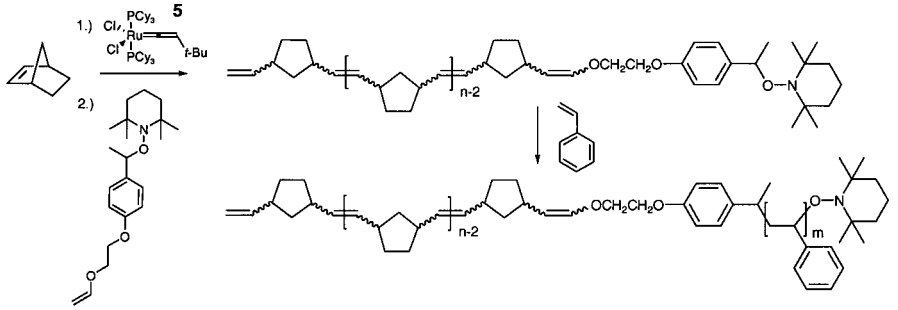


Figure 7

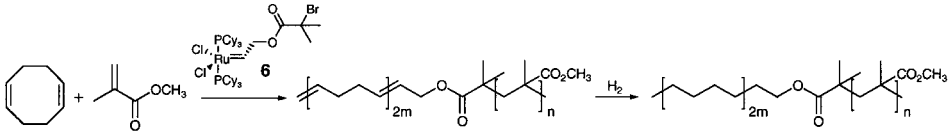


Figure 8

Another work of Bielawski et al. deals with the synthesis of poly(styrene)-*b*-poly(butadiene)-*b*-poly(styrene) and poly(methyl methacrylate)-*b*-poly(butadiene)-*b*-poly(methyl methacrylate) block copolymers using the ROM polymer as telechelic macroinitiator for the heterogeneous atom transfer radical polymerisation (Figure 9) [39]. The synthesised block copolymers showed PDIs between 1.3 and 1.7. A similar approach was published by Katayama et al. [40].

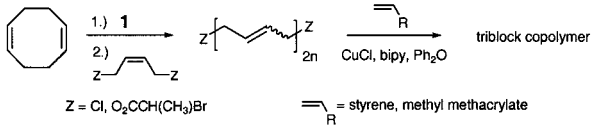


Figure 9

Surface Modified Materials

Ring-opening metathesis polymerization has been successfully introduced for the synthesis of a large variety of tailor-made supports suitable for solid-phase extraction (SPE) [41], capillary electrophoresis (CE) [42], high-performance liquid chromatography (HPLC) [43] as well as hyphenated techniques [44] by the group of Buchmeiser. Functionality, polarity or capacity of the column materials could be tuned by the different architectures of the polymer, which is coated or grafted onto the support [45].

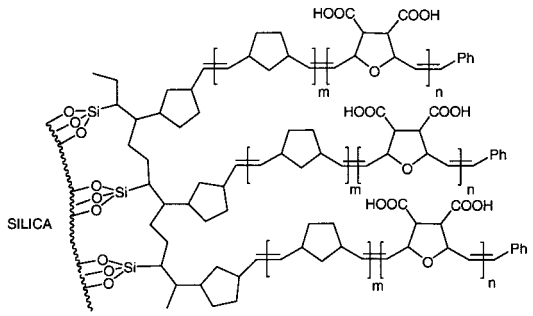


Figure 10: Schematic representation of poly(7-oxanornorn-2-ene-5,6-dicarboxylic acid)-*b*-poly(norborn-2-ene) coated onto silica

Nanoclusters

ROMP block copolymers also can serve as nanoreactors for the synthesis of nanoclusters. $CoFe_2O_4$-nanoparticels were synthesized even at room temperature making use of microphase separation of a diblock copolymer (Figure 11) [46]. The strategy avoids the need of extremely high temperatures necessary in conventional synthesis of these nanoparticles.

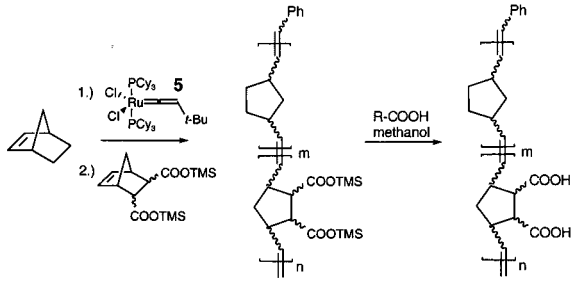


Figure 11

The same method was also used to prepare ZnO nanoparticles [47]. Furthermore, ROMP was used to modify soluble gold nanoparticles with redox-active polymers (Figure 12) [48]. A star-shaped unimolecular amphiphilic block copolymer was prepared and utilized for controlled templating of silsesquioxanes during thermal curing [49].

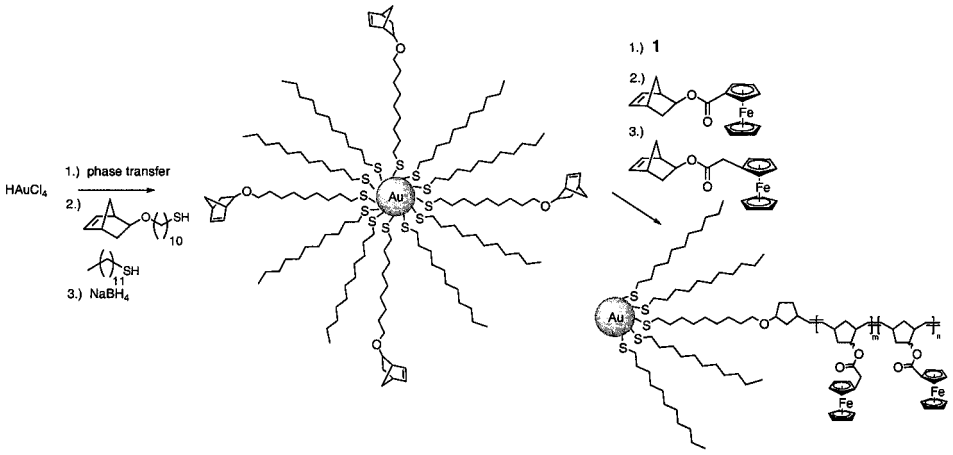


Figure 12

Macromonomers

Another interesting field of polymer science is the synthesis of highly branched polymers. One important class of these are poly(macromonomers), which can be easily obtained using ROMP (Figure 13) [50].

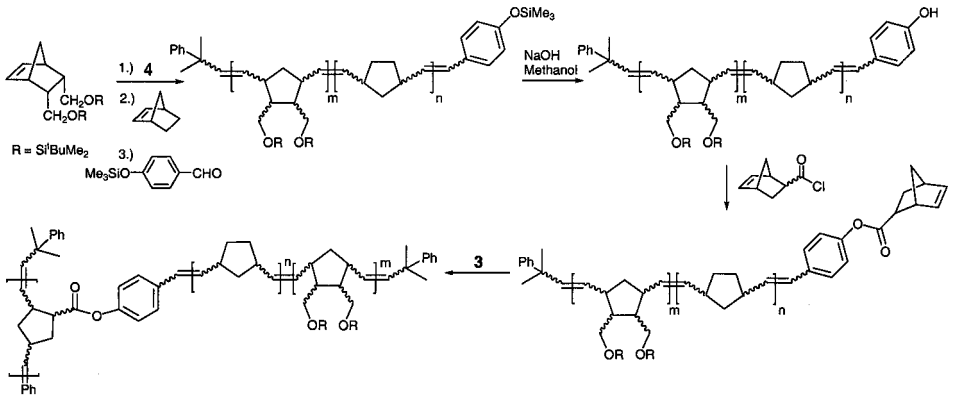


Figure 13: Schematic representation of a macromonomer and the poly(macromonomer)

Miscellaneous Applications

Block copolymers containing linear poly(ethylene) blocks have been of interest for at least 40 years already [51], although poly(ethylene) block copolymers prepared with Ziegler catalyst retain broad molecular weight distributions, complicating the elucidation of their structure.

The most successful route for the preparation of linear poly(ethylene) and its block copolymers with narrow molecular weight distribution is ROMP of monocyclic alkenes, followed by a hydrogenation step. Trzaska et al. reported the synthesis of poly(ethylidenenorbornene)/poly(cyclopentene) diblock copolymers using initiator **4** at room temperature in the presence of trimethylphosphine with a PDI below 1.1. (Figure 14) [52].

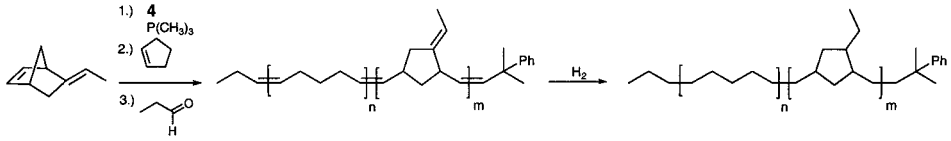


Figure 14

Block copolymers with the 3rd generation Grubbs initiator

As has been emphasized in the introduction an initiator providing high activity, complete initiation, high functional group tolerance and low sensitivity towards moisture and oxygen could revolutionize the field of block copolymer synthesis using ROMP. Indeed, pyridine derivative containing ruthenium complexes of the type depicted in Fig. 15 were found to fulfil the desired profile. Initiator **7** was prepared by Grubbs et al. [53] and identified as a fast initiating initiator by our group in 2002 [54]. More recently Love et al. introduced $(H_2IMes)(Cl)_2(3\text{-bromopyridine})_2Ru{=}CHPh$ (**8**), which was stated to initiate even at a higher rate than **7** [55].

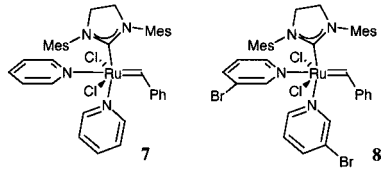
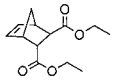
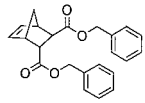
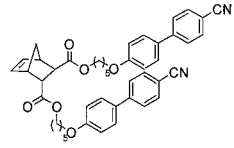
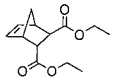
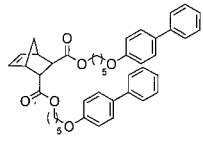
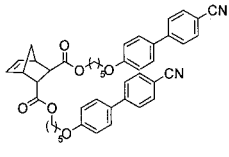
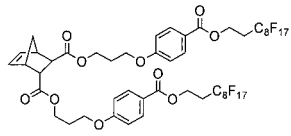
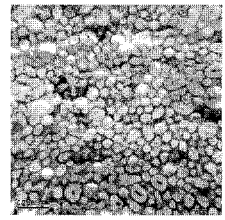
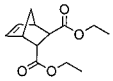
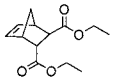
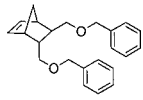
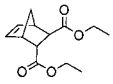
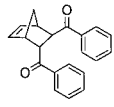
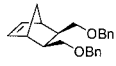
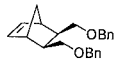
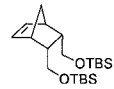
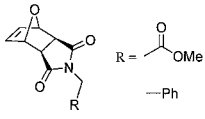
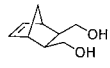


Figure 15: Initiators **7** and **8**

Since then the so called 3rd generation Grubbs initiator **8** and also initiator **7** have been tested for their potential in block copolymer synthesis. Both initiators provide complete initiation and an outstanding functional group tolerance, which was proven by our group using a combination of matrix-assisted laser desorption/ionisation mass spectroscopy, gel permeation chromatography and NMR spectroscopy on an ABC triblock cooligomer (Table 3: entry 1) [56]. Table 3 summarizes examples of different monomers, which were used to synthesise

Table 3: ROMP of various monomers with catalyst **7** including a TEM image of the block copolymer in entry 3 (monomer 1/monomer 2 = 3/1)]

Entry	Monomer 1	Monomer 2	Monomer 3	PDI
1[56]				1.17
2[57]				1.08
3[57]				1.20
4[57]				1.13
5[57]				1.10
6[57]				1.08
8[58]				1.07
9[58]				1.05
10[59]				-

well defined block copolymers with initiators **7** or **8** [57,58,59]. A 3:1 block copolymer of the monomers listed in table 3, entry 3 showed lamellar and spherical phase separation in the microscopic scale. A corresponding TEM image is included in the table.

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