Simple Synthesis of Poly(acetylene) Latex Particles in Aqueous Media

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forward synthetic methods are essential to allow comercialization.

In contrast to 1-alkyne polymerization, the cyclopolymerization of 1,6-heptadiynes offers attractive access to poly(acetylene)s with cyclic recurring units along the backbone, where 1,3-interactions of the substituents, which are responsible for low effective conjugation lengths in poly(1-alkyne)s, are absent.[7,8] Poly(acetylene)s obtained by cyclopolymerization display good solubility in common organic solvents such as benzene, toluene, dichloromethane, and chloroform, good long-term stability towards oxidation, and low energy transitions between the valence and conductivity bands.[7–10] They can be synthesized by using Ziegler catalysts,[11,12] Pd catalysts,[13] anionic polymerization,[14] or binary/ternary Mo or W catalysts.[15] Well-defined molybdenum carbenes in high oxidation states (Schrock catalysts **I**, Figure 1) must be

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Since the discovery of the conductive properties of poly(acetylene),[1–3] conjugated polymers have been widely used in organic light-emitting diodes (OLEDS), solar cells, photovoltaic devices, field-effect transistors, and lasers.[1–6] Despite significant improvements, materials derived from poly(acetylene)s still suffer from certain drawbacks from a technical point of view. These include insufficient stability and processability, poorly defined composition in terms of connectivity, end groups, and molecular weight, and difficult synthetic accessibility. Any successful application of these systems requires a high degree of definition and variability in monomer structure and depends on the stability and processability of the final polymeric material. Furthermore, straight-
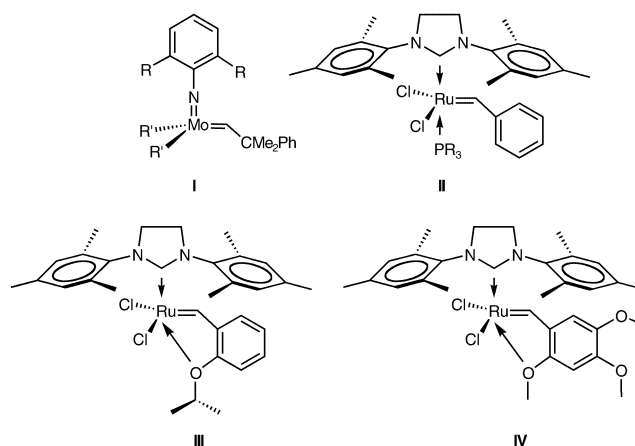
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Figure 1. Schrock catalysts **I**, Grubbs–Herrmann catalysts **II**, Grubbs–Hoveyda catalyst **III**, and an asarone-type Grubbs–Hoveyda catalyst **IV**.

regarded as superior since they cyclopolymerize 1,6-heptadiynes in a living manner[15,16] and can be tuned so that only one single repeat unit, for example, 1,3-(cyclopent-1-enylene)vinylenes[17,18] or 1,3-(cyclohexen-1-enylene)methylidenes,[9,10] is obtained. Despite their unique catalytic properties, the strictly air- and moisture-free conditions that are required for the use of Schrock catalysts are a major limitation to technically relevant applications.

Therefore, for any technological use these systems have to be synthesized by more straightforward routes. Grubbs–Herrmann catalysts (e.g. [RuCl₂(=CHC₆H₅)(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene)(PCy₃)], **II**, Figure 1) and Grubbs–Hoveyda catalysts (e.g. [RuCl₂(=CH-(2-(2-PrO)-C₆H₄))(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-yliden)], **III**, **IV**)[19] are air- and moisture-stable metathesis catalysts with remarkable activity, sometimes rivaling that of highly active Schrock catalysts.[20] Despite their activity in ring-opening metathesis polymerization (ROMP) as well as ring-closing, enyne, and ring-opening cross metathesis reactions, none of the existing systems is capable of polymerizing alkynes or cyclopolymerizing 1,6-heptadiynes. Poly(acetylene)s can, in principle, be prepared

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with these catalysts, but ROMP-based routes are required.[21] The synthesis presented herein of a modified Grubbs–Hoveyda catalyst that can accomplish the cyclopolymerization of 1,6-heptadiynes in both a living and stereoregular way now closes the gap between molybdenum and ruthenium metathesis catalysts.

The reaction of [RuCl$_2$(=CH-(2-(2-PrO)-C$_6$H$_4$)(1,3-dimesityl-4,5-dihydroimidazolin-2-ylidene)] with two equivalents of silver trifluoroacetate provided [Ru(CF$_3$COO)$_2$(=CH-(2-(2-PrO)-C$_6$H$_4$)(1,3-dimesityl-4,5-dihydroimidazlin-2-ylidene] (**1**, Scheme 1).[22] The enhanced polarization across the Ru−C

double bond directly translates into an increased reactivity, thus allowing the cyclopolymerization of diethyl dipropargyl-malonate (DEDPM). Interestingly, none of the existing Ru metathesis catalysts, such as [RuCl$_2$(=CH-(2-(2-PrO)-C$_6$H$_4$)(NHC)], [RuCl$_2$(=CHC$_6$H$_5$)(PCy$_3$)(NHC)] (PCy$_3$ = tricyclohexylphosphane, NHC = 1,3-dimesitylimidazolin-2-ylidene, 1,3-dimesityl-4,5-dihydroimidazlin-2-ylidene), [RuCl$_2$(=CH-(2-(2-PrO)-C$_6$H$_4$)(1,3-dimesitylimidazolin-2-ylidene)], or [RuCl$_2$(=CH-(2,4,5-(MeO)$_3$-C$_6$H$_2$))(1,3-dimesityl-4,5-dihydroimidazolin-2-ylidene)], is reactive enough to accomplish this task. Although it is highly active, **1** did not allow a living polymerization of DEDPM.[23]

Irrespective of stoichiometry, polymers with molecular weights of about 12 000 g mol^{-1} were obtained (Table 1, entries 1, 2). The ratio of the rate constants for propagation and initiation (k_p/k_i)[24] was greater than 1000, which indicated the negative role of the 2-(2-propoxy)benzylidene ligand. Exchange by the 2,4,5-trimethoxybenzylidene ligand[25] led to the formation of [Ru(CF$_3$COO)$_2$(=CH-(2,4,5-(MeO)$_3$-C$_6$H$_4$))(1,3-dimesityl-4,5-dihydroimidazolin-2-ylidene)] (**2**). This complex turned out to be an excellent catalyst for the cyclopolymerization of DEDPM, as it allowed full control over the molecular weight. Thus, polymerizations of DEDPM initiated with **2** in dichloromethane proceeded in a class VI living manner (Figure 2).[26] Excellent agreement between the theoretical and experimentally determined molecular weights was observed. For all polymers the polydispersity index (PDI) was less than 1.65. The value for k_p/k_i was 3, thus indicating a well-behaved system. In fact, the polymerization system **2**/DEDPM was living
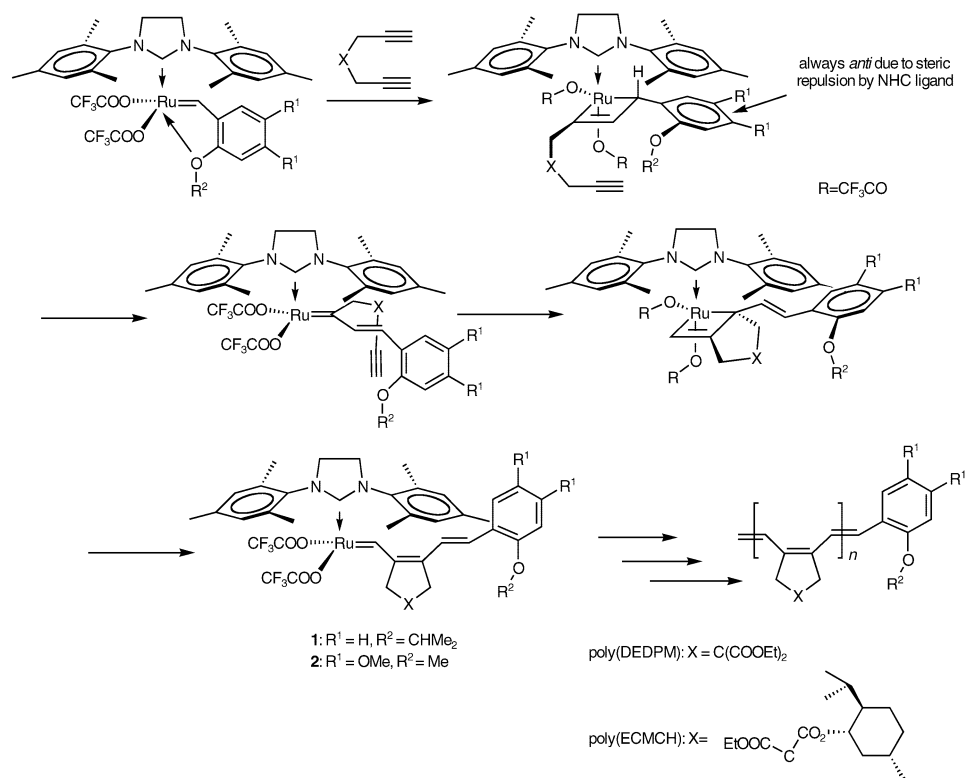
Scheme 1. The *trans* selectivity and stereoselectivity in the cyclopolymerization of DEDPM.

Table 1: Results of the polymerization with catalysts **1–4**.[a]

Poly(acetylene)	Cat.	Solvent	M_n (theor.)	M_n (LS)	M_w (LS)	PDI (LS)	n (LS)	λ_{max} [nm]	E [eV]
poly(DEDPM)$_{100}$	1	CH$_2$Cl$_2$	11 975	10 400	16 800	1.62	43	584	2.123
poly(ECMCH)$_{50}$	1	CH$_2$Cl$_2$	17 485	11 100	28 700	2.59	32	586	2.116
poly(DEDPM)$_5$	2	CH$_2$Cl$_2$	1 389	5 600	7 300	1.30	23	573	2.164
poly(DEDPM)$_{10}$	2	CH$_2$Cl$_2$	2 571	7 000	11 000	1.57	29	576	2.153
poly(DEDPM)$_{30}$	2	CH$_2$Cl$_2$	7 296	13 100	21 400	1.63	55	578	2.145
poly(DEDPM)$_{50}$	2	CH$_2$Cl$_2$	12 021	16 200	26 400	1.63	68	580	2.138
poly(DEDPM)$_{70}$	2	CH$_2$Cl$_2$	16 747	20 000	22 000	1.10	84	583	2.127
poly(DEDPM)$_{100}$	2	CH$_2$Cl$_2$	23 835	27 500	42 400	1.54	116	584	2.123
poly(ECMCH)$_{50}$	2	CH$_2$Cl$_2$	17 517	13 000	22 400	1.72	37	586	2.116
poly(DEDPM)$_{50}$	3	H$_2$O	11 975	7 700	16 000	2.08	32	584	2.123
poly(ECMCH)$_{50}$	3	H$_2$O	17 485	8 100	10 400	1.28	23	584	2.123
poly(DEDPM)$_{50}$	4	H$_2$O	12 021	9 500	13 100	1.38	40	580	2.138
poly(DEDPM)$_{100}$	4	H$_2$O	23 835	12 700	15 600	1.23	53	584	2.123

[a] LS = light scattering, n = degree of polymerization, λ_{max} = UV/Vis absorption maximum, E = energy gap between the valence and conductivity bands; molecular weights in g mol^{-1}. The polymers were obtained in virtually quantitative yields (>95%).
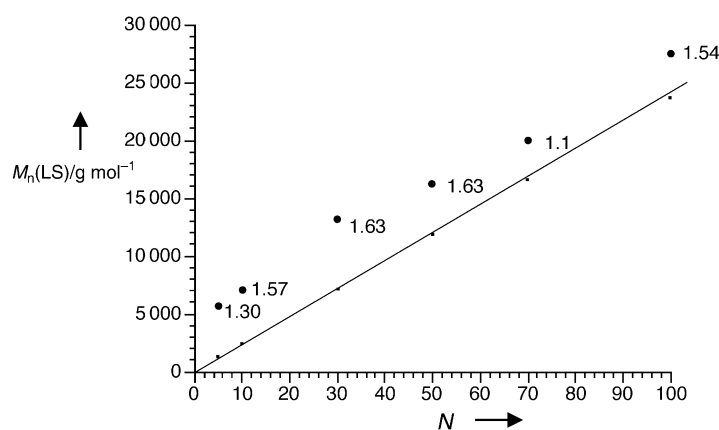
Figure 2. The living character of the polymerization of DEDPM with **2**. N = number of monomer equivalents added; solid line: theoretical values.

even after two days, as shown by the stepwise addition of monomer.

Interestingly, the unsaturated analogue of **1**, [Ru(CF$_3$-COO)$_2$(=CH-(2-(2-PrO-C$_6$H$_4$))(1,3-dimesitylimidazol-2-yl-idene)] was totally inactive. Keeping in mind all the (sometimes incremental) changes that have been made in the original first-generation Grubbs catalyst, [RuCl$_2$-(=CHC$_6$H$_5$)(PCy$_3$)$_2$], or the Herrmann catalyst, [RuCl$_2$(=CHC$_6$H$_5$)(NHC)$_2$] (NHC = 1,3-dimesityl-imidazolin-2-ylidene), these results illustrate the drastic effects of even small changes in the ligand sphere of a catalyst.

In terms of microstructure, poly(DEDPM) prepared with **1** or **2** consists virtually solely (> 95 %) of 1,3-cyclopent-1-enylenevinylene units, as shown by ^{13}C NMR spectroscopic measurements.[17,18] Energy band gaps were calculated from the absorption maximum (λ_{max})[27] and are summarized in Table 1. The polymerization mechanism certainly follows that of molybdenum-catalyzed cyclopolymerizations and is shown in Scheme 1.[7]

Upon addition of DEDPM to **1**, signals corresponding to the first insertion products at δ = 15.63, 18.67, 19.90, 20.84, and 21.63 ppm were observed in the ^{1}H NMR spectrum. The high *trans* selectivity of the vinylene groups probably originates from the steric repulsion of the 2-(2-PrO-C$_6$H$_4$) groups and the growing poly(acetylene) chain by the NHC ligand. In contrast, the selective insertion is most likely governed by the steric demands of the carboxylate groups. A conformation of the intermediate ruthenacyclobutene with one carboxylate ligand in a *trans* orientation with respect to the NHC ligand was assumed[28] and fits the stereochemical data.

By using MALDI-TOF mass spectrometry, 2-propoxy-benzylidene was found to be the end group in polymers prepared with **1**, which indicates the absence of any chain-transfer reactions. In no case was backbiting observed. The polymerization of the chiral 4-(ethoxycarbonyl)-4-(1*S*,2*R*,5*S*)-(+)-menthoxycarbonyl-1,6-heptadiyne (ECMCH, Scheme 1) by **1** proceeded in a stereo- and regioselective manner to

provide tactic poly(*trans*-1,3-(cyclopent-1-enylene)vi-nylene) with greater than 95 % stereoregularity, as shown by ^{13}C NMR spectroscopy.[17,18] This finding is of particular interest, since polymers prepared by ROMP by using other Ru catalysts revealed a *trans* content of 90 % or less and low stereoregularity.[20,29]

One of the advantages of ruthenium-based catalysts is their tolerance to polar functional groups and water as a reaction medium. Polyenes that are synthesized in the form of stable aqueous dispersions are particularly attractive for many industrial applications, since they can be directly deposited on suitable supports such as clays. We therefore tried to establish a system capable of polymerizing DEDPM under aqueous conditions and providing stable latices in a single step. The use of **1** in combination with micelle-forming compounds such as sodium dodecylsulfate (SDS) resulted only in the formation of oligomeric precipitates. As an alternative, the amphiphilic poly(2-oxazoline)-derived block copolymer Me$_{30}$Non$_6$(PenOH)$_2$Pip, which is known to undergo micellization in water,[30] was synthesized by living cationic polymerization (Scheme 2).[31] Again, its use with **1** only resulted in oligomeric precipitates. We therefore focused on fixation of the catalyst on the micelle-forming, amphiphilic block copolymers.
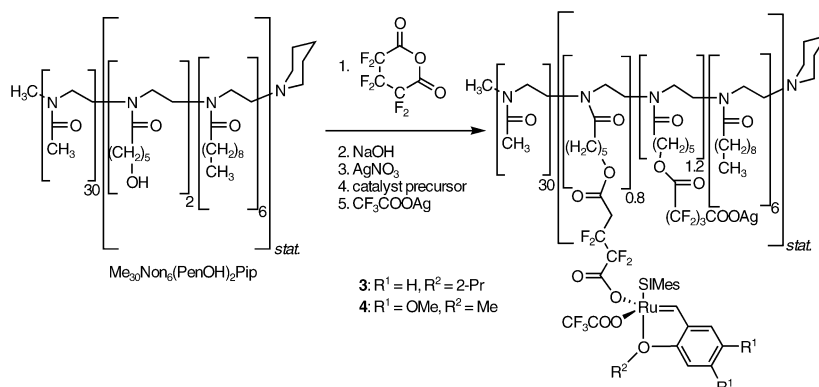
Scheme 2. Immobilization of [RuCl$_2$(=CH-2-(2-PrO-C$_6$H$_4$))(SIMes)] on poly(2-oxazoline)-based block copolymers. SIMes = 1,3-bis(2,4,6-trimethylphenyl)4,5-dihydroimidazolin-2-yli-dene.

The synthesis of a polymer-bound catalyst had to fulfill two requirements: On one hand, perfect mimics of **1** and **2** had to be generated to maintain their reactivity and stereo-selectivity. On the other hand, and in contrast to any suspension or emulsion polymerization, the catalyst had to be *permanently* linked to the block copolymer. The catalyst is best located in the hydrophobic micellar core, where, upon micelle formation of the functionalized block copolymer, the monomer will also be dissolved. The functionalized block copolymers were prepared by allowing Me$_{30}$Non$_6$(PenOH)$_2$-Pip, which bears two randomly distributed hydroxy groups in the side chain of the hydrophobic block, to react with hexafluoroglutaric anhydride. Subsequent deprotonation with aqueous NaOH and reaction with Ag(NO$_3$) yielded the

corresponding polymer-bound silver carboxylate. The last steps involved reaction with the catalyst precursors, [RuCl₂-(=CH-2-(2-PrO)-C₆H₄)(1,3-bis(2,4,6-trimethylphenyl)-4,5-di-hydroimidazolin-2-ylidene)] and [RuCl₂(=CH-2,4,5-(OMe)₃-C₆H₂)(1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazolin-2-ylidene)],[25] respectively, followed by reaction with silver trifluoroacetate to replace the second, unchanged chloride ligand of the catalyst. In the course of this two-step chloride exchange, the corresponding ruthenium compounds were fixed to the support to yield the poly(2-oxazoline)-immobilized catalysts [Me₃₀Non₆{(PenOCO(CF₂)₃COO)(CF₃-COO)Ru(=CH-2-(2-PrO)-C₆H₄)(SIMes)}₀.₈(PenOCO(CF₂)₃-COOAg)₁.₂Pip] (**3**) and [Me₃₀Non₆{(PenOCO(CF₂)₃-COO)(CF₃COO)Ru(=CH-2,4,5-(OMe)₃-C₆H₂)(SIMES)}₀.₈-(PenOCO(CF₂)₃COOAg)₁.₂Pip] (**4**; Scheme 2).

The catalyst immobilization was followed by ^{1}H NMR spectroscopy (in CD₃OD), which provided exact information on the quality and selectivity of this reaction. The alkylidene protons of the polymer-bound catalyst **3** gave a single signal at $\delta = 17.51$ ppm, which is in excellent agreement with the single signal at $\delta = 17.58$ ppm in the ^{1}H NMR spectrum of the free catalyst. On one hand, the similarity of these two chemical shifts indicates a selective immobilization in which no free catalyst or any other catalytic species was observed. On the other hand, it underlines the degree of similarity between **1** and the supported analogue **3**, even more so as the chemical shift for the alkylidene protons in this type of catalyst is very sensitive towards changes in the ligand sphere. It is noteworthy that a successful immobilization requires both straightforward synthetic routes and the careful design of the block sizes in the amphiphilic copolymer. Whereas the use of Me₃₀Non₄(PenOH)₄Pip resulted in insoluble, catalyst-loaded species, Me₃₀Non₆(PenOH)₂Pip could be successfully used for these purposes.

The quantification of the ruthenium content in **3** and **4** by means of ICP-OES measurements indicated that 40% of the polymeric silver salt had reacted with the catalyst precursors **1** and **2**, which led to ruthenium loadings in the block copolymer of 0.16 mmol g^{-1} upon use of **3** and **4**. For the polymerization of DEDPM with **4**, a value of 11 was found for k_p/k_i. Poly(DEDPM) prepared with **4** in water was characterized by lower polydispersity indices (<1.40) compared to poly-(DEDPM) prepared with **2**.

Owing to the increased concentration of DEDPM within the micelles, the reaction times required to reach complete conversion were reduced to 30 min with **3** and **4** compared to 2 h with **2**. This illustrates the effect of the micellar "nano-reactors" formed in an aqueous medium. Nevertheless, the polymerization itself cannot be regarded as living.

The TEM analysis of the resulting polymer latices revealed particle sizes between 100 and 200 nm, which is typical for an emulsion-based process (Figure 3). Stabilized by the amphiphilic structure of the block copolymer, the latices could be stored for over two weeks without any change in terms of particle size, molecular weight, or UV/Vis absorption maximum. In addition, immobilization of the catalyst allowed separation of the catalyst from the product to obtain virtually Ru-free poly(acetylene)s with a Ru content of 0.35 ppm or less. Poly(DEDPM) prepared by any of the
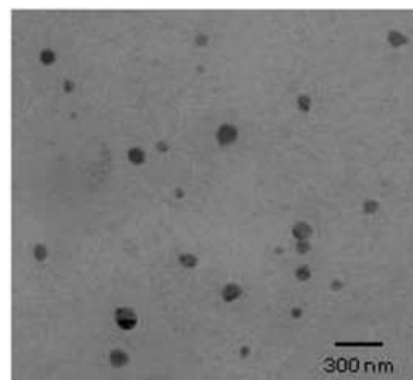

Figure 3. The TEM micrograph of the stable poly(DEDPM) latex particles.

methods reported herein was stable in the solid state under ambient conditions, including in the presence of air and moisture, which is relevant for technical use.

In summary, we have elaborated the first synthetic protocol that allows the preparation of highly conjugated polyenes by cyclopolymerization of 1,6-heptadiynes with a ruthenium metathesis catalyst in a living manner. Furthermore, these polyenes are accessible even under aqueous, micellar conditions. We are convinced that these findings will revitalize poly(acetylene) chemistry and related research areas.

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