Vinylidene-based polymers by Rh(I)-NHC catalyzed thiol-yne click polymerization: Synthesis, characterization and post-polymerization modification

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Complex RhCl(IPr)(pyridine)(η^2 -coe) (IPr = 1,3-bis-(2,6diisopropylphenyl)imidazol-2-ylidene) efficiently catalyzes the polyhydrothiolation of aromatic diynes with aliphatic dithiols to give vinylidene-based polymers (vinylidene content of 80%) with high molecular weights (M_w up to 199 000). These polymers have shown to be chemically modifiable through hydrogenation and chemical oxidation processes.

Click polymerization has emerged as a powerful and highly efficient methodology to construct polymeric materials with novel structures and advanced properties.¹ In particular, the development of alkyne-based polymerization reactions, such as the azide-alkyne² and thiol-based³ click polymerizations, has allowed tailoring polymeric scaffolds with well-defined structures and versatile functions. In fact, thiol-yne click chemistry has become a useful synthetic tool in polymer science enabling both the facile and atom-economic synthesis of sulfur-containing polymers with topological structures and post-polymerization chemical modification.⁴

Alkyne hydrothiolation is a valuable atom-economical transformation for the straightforward synthesis of vinyl sulfides.⁵ However, the chemo-, regio- and stereoselectivity control of the reaction still remains a challenge. Markovnikov thiol addition produces the branched isomer whereas two linear stereoisomers can be formed through the anti-Markovnikov addition route.⁶ From a mechanistic point of view, thiol-yne click reaction can be triggered by photo- and thermo-initiated free radicals, organic and inorganic bases or metal-based catalysts.⁷ In this context, rhodium complexes have revealed as chameleonic species with the potential to direct the regioselectivity upon subtle tuning of the ancillary ligands.^{8,9}

Photo-induced thiol-yne click polymerizations activated by UV irradiation usually yields sulfur-containing insoluble materials with hyperbranched structures resulting from the double addition of the thiol to the alkyne.¹⁰ In contrast, transition

metal-catalyzed thiol-yne and nucleophile-mediated thiolactivated alkyne click polymerizations stop at the vinyl sulfide stage instead to proceed to alkyl sulfide.^{11, 12} Thus, a series of electronically active poly(vinylene sulfide)s have been synthesized from a range of aromatic divnes and dithiols. Wilkinson's catalyst, RhCl(PPh₃)₃, affords stereoregular linear poly(vinylene sulfide)s with *E*-conformation¹¹ whereas polymers.12 secondary amines produces Z-enriched Interestingly, thiol-yne click polymerization can be also propagated spontaneously without catalysts or external stimuli via a free-radical process to give linear and hyperbranched poly(vinylene sulfide)s (Figure 1).¹³



Figure 1. Control of the regioselectivity in thiol-yne click polymerization.

We have recently developed a series of Rh^I(NHC)-based catalyst precursors (NHC, N-heterocyclic carbene) for the Markovnikov-selective hydrothiolation of alkynes to give the challenging α -vinyl sulfide products under mild reaction conditions.⁹ In particular, the system $[Rh(\mu-Cl)(IPr)(\eta^2$ coe)]₂/pyridine has shown an outstanding catalytic activity with excellent selectivity towards branched α -vinyl sulfides. The responsible species for the catalytic activity is the mononuclear RhCl(IPr)(py)(η^2 -coe) (1) complex resulting from the bridge-cleavage by pyridine. In fact, both species are in equilibrium rendering the concentration of pyridine essential for the control of regioselectivity.^{9d} In light of these precedents, we wondered about the potential of 1 for the preparation of poly(vinylidene sulfide)s by regioselective thiolyne click polymerization. Interestingly, polymers containing vinylidene moieties (=CH₂) included in the backbone are really scarce. These materials have been prepared in two principal

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ways, by polymerization of monomers pre-containing an exomethylene group,¹⁴ or by a reaction that provides =CH₂ in the skeleton of the polymer.¹⁵ Only few examples of this second case have been studied, among these, the stereospecific reaction of diyne leading to poly-enynes with vinylidene linkages, or the polycondensation between propargyl carbonates and bisphenols. Remarkably, to the best of our knowledge, the synthesis of poly(vinylidene sulfide)s via rhodium-catalyzed hydrothiolation have not been reported so far.



Given the solubility problems associated to the copolymerization of rigid building blocks, we envisage the combination of rigid aromatic diyne monomers, 1,3- (a) and 1,4-diethynylbenzene (b), with the flexible 1,6-hexanedithiol (2) (Scheme 1). The polymerization reactions were carried out in THF at room temperature using 1-2 mol% of catalyst 1 formed in situ from $[Rh(\mu-Cl)(NHC)(\eta^2-coe)]_2$ and a ten-fold excess of pyridine. The reactions were monitored in situ by ¹H NMR spectroscopy and SEC-MALS on aliquots of freshly made polymer solutions. Reaction of 1,3-diethynylbenzene (a) with 1,6-hexanedithiol (2) in the presence of 1 mol% of catalyst 1 for 24 h gave polymer 2a. The polymer exhibited a bimodal molecular weight distribution with a light fraction (M_w = 5 500, 23%) and a main fraction of higher molecular weight (M_w = 33 300, 77%) and a polydispersity index (M_w/M_n) of 2.25 (Table 1, entry 1). Delightfully, the vinylidene content (α) of the polymer determined by ¹H NMR was 77%. Increasing the catalyst loading to 2 mol% also gave a polymer with a bimodal distribution with a main fraction of higher molecular weight, $M_{\rm w}$ = 42 200, lower polydispersity ($M_{\rm w}/M_{\rm n}$ = 1.78) and a vinylidene content of 80% (entry 2).

Polymer **2b** was obtained by co-polymerization of 1,4diethynylbenzene (**b**) and 1,6-hexanedithiol (**2**) under the same reaction conditions. A polymer with a unimodal SEC profile of M_w = 46 900, narrow polydispersity (M_w/M_n = 1.85) and a vinylidene content of 80% was obtained using a 1 mol% of rhodium catalyst after 24 h (entry 3). The molecular weight of the polymer increased up to 199 000 after 48 h while maintaining the polydispersity (entry 4). However, the increase of the catalyst loading to 2 mol% gave a polymer of lower M_w and very narrow polydispersity, M_w = 20 200 and M_w/M_n = 1.27 in 24 h, whose mass increased up to M_w = 72 500 after 48 h (entries 5 and 6).

Table 1. Click polymerization of 1,6-hexanedithiol (2) with 1,3- (a) and 1,4-diethynylbenzene (b) catalyzed by $[Rh(\mu-CI)(coe)(IPr)]_2/py$.^a

Entry	Polym.	1 ^ь (mol%)	t (h)	<i>M</i> _w ^c	$M_{\rm w}/M_{\rm n}^{\rm c}$	% ^d	α/β -E ^e
1	2a	1	24	3.33E+04	2.25	77	3.3
				5.50E+03	1.05	23	
2	2a	2	24	4.22E+04	1.78	80	4.0
				4.70E+03	1.11	20	
3	2b	1	24	4.69E+04	1.85		4.0
4	2b	1	48	1.99E+05	1.86		
5	2b	2	24	2.02E+04	1.27		4.0
6	2b	2	48	7.25E+04	1.29		

^a Reactions were carried out in THF (2.5 mL) at 25 °C, [**2**] = [diyne] = 0.25 M. ^b mol% of catalyst RhCl(coe)(IPr)(py) (**1**) formed in situ, [Rh] = 2.51-5.02 mM. ^c Estimated by SEC-MALS in THF, M_w = weight-average molecular weight, M_n = number-average molecular weight, M_w/M_n polydispersity index (PDI). ^d Bimodal distribution, weight percentage of each fraction. ^e Ratio between vinylidene (α) and *E*-vinylene (β -*E*) groups determined by ¹H NMR.

These data suggest that the trans disposition of the alkynyl functions results in a more efficient polyhydrothiolation which allows to prepare high molecular weight polymers. On the other hand, the high catalytic activity of **1** in combination with a high catalyst loading affords larger oligomers what makes the growth of the polymer more difficult thereby resulting in lower M_w polymers.

The ¹H NMR spectra of both polymers showed two set of resonances characteristic for the vinylidene and vinylene groups. The exo-methylene protons (=CH₂) were observed as two well separated resonances around δ 5.5 and 5.1 ppm, whereas several ABq with J_{AB} coupling constants of 12-16 Hz were observed for the =CH resonances of the vinylene groups around δ 6.6 ppm, which is in agreement with an E configuration. The α/β -*E* ratio of the polymers, determined by integration of both set of resonances, is lower than that found in the hydrothiolation of phenylacetylene with 1,6hexanedithiol (2) as model reaction (4.0 vs 7.3), which gave the divinyl-sulfide products: α - α (88%) and α - β (12%), with only trace amounts of the β - β product.^{9d} Thus, if a set of three vinyl sulfide units is considered, as the occurrence of two adjacent β -vinyl sufide units is unlikely, the following three arrangements α - α - α , α - β - α and β - α - β , could account for the polymer chain structure.[‡] This analysis is compatible with the observation of three ABq of different intensity for the =CH resonances of the vinylene groups (β -*E*) in the ¹H NMR spectra of 2b (see ESI).

The high vinylidene content into the polymer is explainable taking in account the reaction mechanism of our Rh(NHC)based catalytic system (Figure 2).^{9d} Catalyst **1** reacts with dithiols by S-H oxidative addition providing a Rh^{III} hydride thiolate specie (**b**). This compound can react with alkynes through a 1,2-insertion of the unsaturated moiety into the Rh-S bond giving the branched alkenyl-Rh^{III}-hydride **c**. The final reductive elimination of the alkenyl group with hydride produce α -vinylidene polymer, with the regeneration of **1**. The formation of **c** represents the key step for the selectivity of the

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reaction. In fact, the eventual insertion of the alkyne into Rh-H bond gives rise to a linear alkenyl-Rh^{III}-hydride complex that produces *E*-vinylene products. As we demonstrated the synergist effect of the IPr and pyridine on the metal center allows the selective formation of **c** and the consequent production of vinylidene-based polymers.



Figure 2. Proposed catalytic cycle for the polyhydrothiolation of diynes with dithiols.

The isolation of the polymers has proven to be difficult. The attempts to precipitate them from freshly prepared solutions gave intractable grey-white gummy materials. However, we have found that the addition of THF to the residue obtained after removing the solvent and drying under vacuum for 48 h, affords the polymers as orange-brown fiber-shape jelly-like materials (Figure 3). The obtained gels were dried under vacuum for 48 h to give the polymers as insoluble solids that retain the morphology of the respective materials. Following this procedure, polymers 2a and 2b were obtained as yelloworange fibers and orange-brown sheets and fibers, in 42 % and 71 % yield, respectively. Field-emission scanning electron microscopy (FE-SEM) measurements on the polymers show that the fibrillar network is composed of rolled-sheets (Figure 1). In addition, energy-dispersive X-ray spectroscopy (EDX) analysis has shown the absence of rhodium that could remain as catalyst leftovers in the polymer samples.

Isolation of the polymers in the presence of 2,6-di-tert-butyl-4methylphenol (BHT) did not affect neither the polymer morphology nor the isolated yield thereby excluding a freeradical induced cross linking of the polymer chains. In fact, the IR spectrum of both polymers showed two absorptions at 1679 (s) and 1594 (m) cm⁻¹ for **2a** and, 1671 (s) and 1586 (m) cm⁻¹ for **2b**, associated with C=C stretching vibration of the vinylidene and vinylene groups, respectively.¹⁶ TGA analysis showed that, in spite of structural similarity, polymers 2a and 2b exhibit very different degradation temperatures, 300 and 266 °C respectively. However, the 1st derivative of the weight loss curve for 2b showed a local maximum at 165 °C that was attributed to the presence of occluded solvent (see ESI). Attending to the temperature for the maximum degradation rate, 2a is thermally slightly more stable than 2b (322 and 299 °C, respectively).

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Figure 3. Representative photograph and FE-SEM image of polymer 2a

The DSC thermograms recorded during the first heating cycle exhibited a broad exothermic peak that was not detected in the subsequent scans (see ESI). This peak, centered at 137 and 154 °C for **2a** and **2b** respectively, was ascribed to thermally induced olefin polymerization leading to cross-linking of polymer chains.¹¹

Post-polymerization modification is a smart and versatile synthetic approach to functional materials.¹⁷ The new polymers have reactive and accessible exo-methylene groups along the polymer chain susceptible for chemical modification (Scheme 2). In order to explore the potential for postpolymerization modification, a preliminary reactivity study has been carried out. The vinylidene groups of 2b can be selectively hydrogenated in the presence of Wilkinson's catalyst. After careful removing the excess of pyridine under vacuum, a freshly made solution of 2b in THF was stirred under $H_2(g)$ (5.5 bar) in the presence of RhCl(PPh₃)₃ (5 mol%) at 25 °C for 5 days to give a light orange solution of polymer 2b/h which was isolated as an orange oil. The ¹H NMR spectrum in CDCl₃ in the vinyl region shows exclusively a set of resonances centered at δ 6.57 ppm for the *E*-vinylene fragments thereby confirming the hydrogenation of the vinylidene groups (see ESI). The difference in reactivity of vinylidene and E-vinylene groups can be rationalized in terms of steric effects on olefin binding to the catalyst. Interestingly, the very different relative rates for hydrogenation of alkenes has been used for selective alkene hydrogenation in polyene compounds.¹⁸ The molecular weight of **2b/h** determined by SEC-MALS, $M_w = 2.19E+04$, is about half than that of the vinylidene-based polymer precursor 2b. In addition, the increase of the polydispersity index (M_w/M_n) up to 2.59 suggests the hydrogenolysis of the polymer chain. However, the degradation of the polymer in solution after so long reaction time cannot be ruled out.

The oxidation of the sulfur-rich polymers was explored with the purpose of modifying the electronic character of the vinylidene groups.¹⁹ Reaction of **2b** with 3-chloroperbenzoic acid (MCPBA) in CH₂Cl₂ for 24 h gave a yellow solution from which the vinylidene-sulfoxide based polymer **2b/ox** was isolated as a yellowish solid in 84% after the appropriate workup. The IR spectrum of **2b/ox** showed a strong absorption at 1030 cm⁻¹ characteristic for the S=O stretching of the sulfoxide groups. In addition, no absorptions in the region 1350-1100 cm⁻¹ attributable to sulfone groups were observed.¹⁶ Moreover, attempts to synthesize a vinylidene-sulfone based polymer by increasing the amount of MCPBA have been unsuccessful.

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The ¹H NMR in the vinyl region of **2b/ox** showed a set of ABq ($J_{AB} \approx 15$ Hz) centered at δ 7.1 ppm, corresponding to the β -vinyl sulfoxide groups, and four close resonances centered at δ 6.04 for the α -vinyl sulfoxide groups (see ESI). These resonances are downfield shifted compared to that of polymer **2b** which is in agreement with the oxidation of the sulfide groups. The integration of both set of resonances showed a α -vinyl sulfoxide content of 80%, identical to the parent vinylidene-based polymer **2b**. It is noticeable that no resonances for phenyl(alkylsulfinyl)oxirane groups have been observed in the ¹H NMR spectrum. The molecular weight of **2b/ox** determined by SEC-MALS, $M_w = 1.64E+04$, is about one-third of that of the vinylidene-based polymer precursor **2b** showing also a slightly higher polydispersity index of 2.04.

Conclusions

In summary, we have successfully applied the catalytic system $[Rh(\mu-Cl)(IPr)(\eta^2-coe)]_2$ /pyridine for the synthesis of sulfur rich vinylidene-based polymers by using the thiol-yne click methodology. These polymers have shown to be chemically modifiable. The reactive vinilydene groups of these polymers have been selectively hydrogenated by using the Wilkinson's catalyst. Moreover, oxidation of the polymers results in the selective formation of a vinylidene-sulfoxide based polymer.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

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‡ The two first descriptors design the configuration of the vinyl groups at the 1,6-bis(thiovinyl)hexane fragment.

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