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Tailor-made poly(vinylidene sulfide)s by Rh(I)–NHC catalyzed regioselective thiol-yne click polymerization

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ABSTRACT

The [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$/pyridine system efficiently catalyzes the polyhydrothiolation of a series of dialkynes with dithiols, producing sulfur-rich poly(vinylidene sulfide)s with a typical M_w in the range 20.000–124.000 and vinylidene content of 75–87%. A combination of flexible aliphatic dithiols, including 1,6-hexanedithiol and 2,2′-(ethylendioxy)diethanethiol, and the rigid aromatic dithiol 4,4′-thiobisbenzenethiol, with rigid aromatic dialkynes, 1,3-diethynylbenzene and 1,4-diethynylbenzene, and flexible dialkynes, including propargyl ether and 1,7-octadiyne, have been used to prepare poly(vinylidene sulfide)s. The copolymerization of flexible dithiols with rigid aromatic dialkynes or vice versa results in high molecular weight polymers, M_w up to 259.000, with low polydispersities. However, polyhidrothiolation of flexible dialkynes with flexible dithiols is much less efficient and usually results in the formation of oligomers. The interplay of the IPr and pyridine ligands on the RhCl(IPr)(py)(η^2-coe) catalyst, which controls the regioselectivity of the alkyne insertion step towards the branched vinyl sulfide, is key in the preparation of these poly(vinylidene sulfide)s.

1. Introduction

Sulfur-containing polymers have attracted increasing scientific and industrial attention in recent years, both from a synthetic point of view and for their high-tech applications in energy, optical materials, optoelectronic devices and biomaterials [1–2]. The click chemistry concept, established by Sharpless and co-workers, [3] has served as an inspiration for the development of efficient synthetic methodologies for the preparation of functional polymers. Click polymerization provides straightforward access to polymeric materials with great structural diversity due to features such as high atom economy, mild reactions conditions, great functionality tolerance, and selectivity control [4–7]. Thiol-based click polymerization also exhibits remarkable advantages and has become a powerful tool for the preparation of sulfur-containing polymers with well-defined structures and advanced properties [8]. The high reactivity of thiols with a wide range of functional groups under benign conditions has enabled a variety of thiol-X click polymerization reactions, including thiol-ene, thiol-yne, thiol-epoxy, thiol-isocyanate and thiol-halogen clicks, among others [9]. Thiol-X click polymerizations produce a range of materials having thioether linkages that can be chemically modified, for example by selective oxidation into either sulfoxides or sulfones [10–12]. Interestingly, a photocatalytic intermolecular three component thiol–yne–ene coupling reaction involving thiols, alkynes and α-vinylsulfides has recently been reported [13].

Thiol-yne click chemistry has become a useful synthetic tool in polymer science, enabling the facile and atom-economic synthesis of sulfur-containing polymers [14–16]. Thiol-yne click polymerization can be triggered by photo- and thermo-initiated free radicals, organic and inorganic bases, or transition-metal based catalysts [17]. Radical-initiated polymerization usually proceeds via a bis-addition to afford high-density hyperbranched poly(thioether)s resulting from the double addition of the thiol to the alkyne [18–21]. However, poly(vinylsulfide)s with different stereoregularities can be obtained when the reaction proceeds in a mono-addition manner (Fig. 1) [22–24]. The organobase-mediated click polymerization of dithiols and diynes affords highly stereoregular linear poly(vinylene sulfide)s with high *Z*-configuration when using diphenylamine as a promoter [25]. However, complete *Z*-stereoregularity was attained by using the inorganic base K_3PO_4 [26]. In

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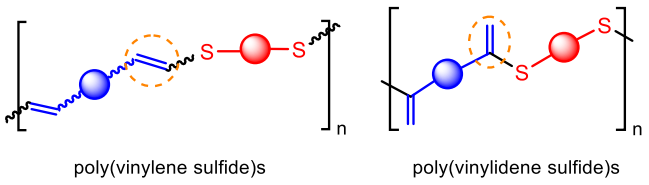


Fig. 1. Regioselectivity in thiol-yne click polymerization.

sharp contrast, thiol-yne click polymerization of dithiols and diynes catalyzed by $RhCl(PPh_3)_3$ selectively affords *E*-stereoregular linear poly (vinylene sulfide)s [27]. 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 [28–29].

We have recently developed a new Rh-catalyzed thiol-yne click polymerization driven by a Rh(I)–NHC (NHC = N-heterocyclic carbene) catalysts that proceeds with Markovnikov regioselectivity. The polyhydroyhiolation of aromatic dialkynes, 1,3-diethynylbenzene and 1,4-diethynylbenzene, with 1,6-hexanedithiol catalyzed by RhCl(IPr)(py)(η^2-coe) (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene) in THF at room temperature afforded unprecedented poly(vinylidene sulfide)s with high molecular weights (M_w up to 199 000) and vinylidene content of 80% (Fig. 1). Interestingly, these poly(vinylidene sulfide)s could be further chemically modified via selective hydrogenation of the vinylidene groups, and oxidation to obtain a poly(vinylidene sulfoxide)s [30]. Polymer containing vinylidene motifs (>C=CH_2) in the backbone are rare. These materials have been prepared by the polymerization of monomers pre-containing an exomethylene group, [31–33] the palladium-catalyzed polycondensation between propargyl carbonates and bisphenols, [34–35] or the dimerization of aromatic diynes [36–37].

The excellent catalytic performance of the catalytic system [Rh(μ-Cl)(IPr)(η^2-olefin)]$_2$/pyridine in the Markovnikov-selective hydrothiolation of terminal alkynes to give the challenging α-vinyl sulfide products [38] and its successful application in the synthesis of poly (vinylidene sulfide)s [30] prompted us to evaluate the applicability of this catalytic system for the preparation of new poly(vinylidene sulfide)s. In this study, we report on the application of the in situ-generated catalyst, RhCl(IPr)(py)(η^2-coe), for the preparation of new poly(vinylidene sulfide)s by expanding the scope of dithiols and dialkynes involved in the polyhydrothiolation reaction. Our results demonstrate the versatility and potential of this catalytic system for the synthesis of a wide range of poly(vinylidene sulfide)s materials with tailored properties.

2. Results and discussion

2.1. The Rh(I)–NHC catalyst.

Transition metal catalyzed addition of an S–H functionality to alkynes is a straightforward and atom-economic transformation for the synthesis of vinyl sulfides. However, controlling the chemo-, regio- and stereoselectivity of the reaction remains a challenge. Markovnikov thiol addition produces the branched isomer, α isomer, while two linear stereoisomers, β-*Z* and β-*E*, can be formed through the anti-Markovnikov addition route (Fig. 2) [39].

We have developed a series of efficient Rh(I)-(NHC) catalyst precursors for the Markovnikov-selective hydrothiolation of alkynes under mild conditions. The dinuclear [Rh(μ-Cl)(IPr)(η^2-olefin)]$_2$ and [Rh(μ-OH)(IPr)(η^2-olefin)]$_2$, [40] as well as the mononuclear Rh(κ^2-N-O)(η^2-olefin)(IPr)[41] (N-O = 8-hydroxyquinolinate) compounds provide access to branched α-vinyl sulfides with excellent selectivity. Moreover, it has been found that Markovnikov-selectivity is usually improved by using pyridine as an additive. Interestingly, the rational design of the Rh(κ^2-N-O)(IPr)(CO) catalyst (N-O = pyridine-2-methanolate) has allowed

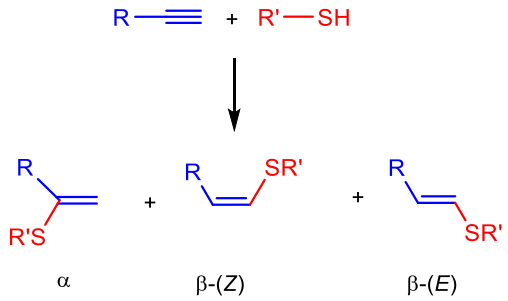


Fig. 2. Possible vinyl sulfide isomers formed in the hydrothiolation of terminal alkynes.

us to improve the selectivity for α-vinyl sulfides without the addition of pyridine [42].

The selection of the most suitable polyhydrothiolation catalyst should considerer both activity and selectivity, as catalyst with moderate activity can lead to the formation of low molar mass polymers. For example, Rh(κ^2-N-O)(IPr)(CO) (N-O = pyridine-2-methanolate) catalysts afforded a 99 % conversion in the hydrothiolation of phenylacetylene with 1,6-hexanedithiol as model reaction in 24 h at 50 °C with a selectivity of 90 % to the α-α divinyl-sulfide product. In contrast, the catalytic system [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$/pyridine achieve almost full conversion in only 0.7 h at 25 °C with a selectivity of 88 % to the α-α product. Therefore, this catalytic system has been chosen for the preparation of poly(vinylidene sulfide)s materials. The dinuclear compound [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ is in equilibrium with the mononuclear RhCl(IPr)(py)(η^2-coe) species in the presence of pyridine,[38] which is proposed to be the catalytically active species, making the concentration of pyridine essential for the control of regioselectivity (Fig. 3).

2.2. Rh(I)-(NHC)-catalyzed polyhydrothiolation of dialkynes with dithiols.

The performance of the catalytic system Rh(μ-Cl)(IPr)(η^2-olefin)]$_2$/pyridine in the preparation of poly(vinylidene sulfide)s by thiol-yne click polymerization has been evaluated using a range of dialkynes and dithiols. Flexible aliphatic dithiols, 1,6-hexanedithiol (**1**) and 2,2′-(ethylendioxy)diethanethiol (**2**), and the rigid aromatic dithiol 4,4′-thiobisbenzenethiol (**3**) have been selected. The chosen dialkynes include rigid aromatic dialkynes, 1,3-diethynylbenzene (**a**) and 1,4-diethynylbenzene (**b**), and the flexible dialkynes propargyl ether (**c**) and 1,7-octadiyne (**d**) (Scheme 1). The polyhydrothiolation reactions were carried out in Schlenk tubes using a solution of 1–4 mol % of catalyst RhCl(IPr)(py)(η^2-coe) in THF under mild reaction conditions (25–50 °C). The catalyst was generated in situ by reaction of dinuclear [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ complex with a ten-fold excess of pyridine. The addition of dithiol preceded that of dialkyne to avoid the self-polymerization of the latter. Although initially the polymerization reactions with dithiol **1** were performed at [dithiol] = [dialkyne] = 0.25 M, more diluted conditions (0.157 M) were used with dithiols **2** and **3** to reduce the viscosity of the resulting polymer solution. The polymerization reactions were analyzed by SEC-MALS on 0.1 mL aliquots of freshly made polymer solutions.

RhCl(IPr)(py)(η^2-coe) efficiently catalyzed the polyhydrothiolation of aromatic dialkynes with 1,6-hexanedithiol (**1**) [30]. The copolymerization of **1** with **a** in the presence of 1 mol% of catalyst for 24 h at 25 °C afforded a polymer **1a** with a bimodal molecular weight distribution with a major fraction of M_w 33.300 (77 %) and a $Đ$ of 2.25. However, copolymerization with **b** under the same conditions gave a polymer **1b** with a unimodal SEC profile of M_w 46.900 and a $Đ$ of 1.85. Interestingly, increasing the reaction time to 48 h resulted in a polymer of M_w 199.000 with similar polydispersity (Table 1, entries 1–3).In sharp contrast, polyhydrothiolation of flexible dialkynes with **1** was much less efficient

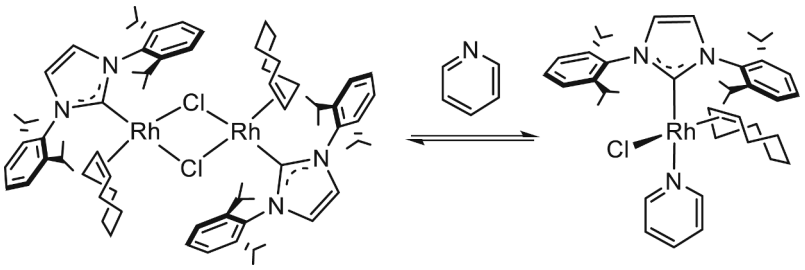
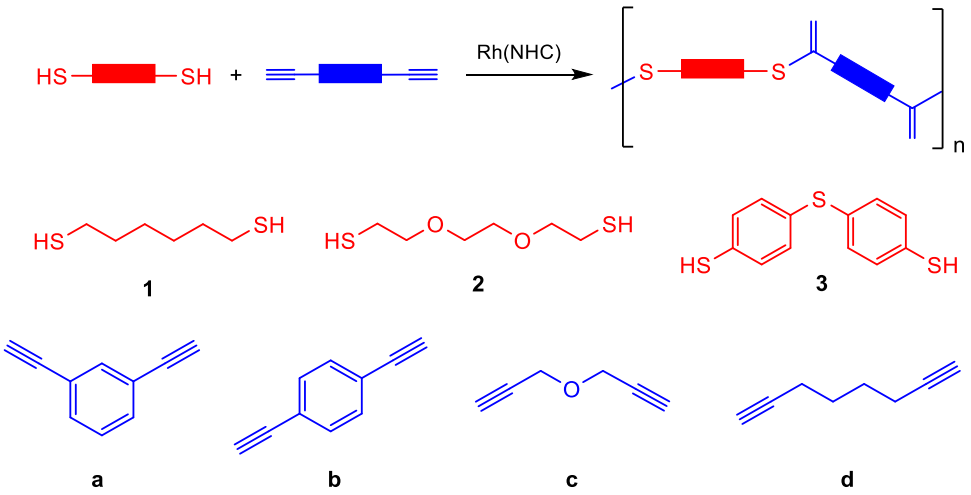


Fig. 3. Pyridine-mediated equilibrium between di-and mononuclear Rh(NHC) species.



Scheme 1. Dithiols and dialkynes used in the preparation of poly(vinylidene sulfide)s.

Table 1
Click polymerization of 1,6-hexanedithiol (**1**) with dialkynes (**a-d**) catalyzed by [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$/py.[a]

Entry	Polymer	mol% Rh[b]	T (°C)	t (h)	M_w[c]	$Đ$ [c]	%[d]	α/β-*E*[e]	Yield (%)[f]
1	**1a**	1	25	24	33.300	2.25	77	3.3	42
					5.500	1.05	23		
2	**1b**	1	25	24	46.900	1.85		4.0	71
3	**1b**	1	25	48	199.000	1.86			
4	**1c**	2	25	72	2.800	1.59			
5	**1c**	4	25	48	9.360	2.57		3.3	70
6	**1d**	4	25	48	1.150	3.94			
7	**1d**	4	40	24	19.300	1.97			
8	**1d**	4	40	48	47.100	2.07	91	1.5	66
					372.000	1.30	9		

[a] Reactions carried out in THF, [dithiol] = [dialkyne] = 0.25 M. [b] mol% of catalyst RhCl(IPr)(py)(η^2-coe) formed in situ, [Rh] = 2.48–10.08 mM. [c] Estimated by SEC-MALS in THF, M_w = weight-average molecular weight, $Đ$ = dispersity (M_w/M_n, M_n = number-average molecular weight). [d] Bimodal distribution, weight percentage of each fraction. [e] Ratio between vinylidene (α) and *E*-vinylene (β-*E*) groups determined by ^{1}H NMR. [f] Isolated yield.

even using a higher catalyst loading. Thus, an oligomer of M_w 2.800 was obtained in the reaction of **1** with **c** using a catalyst loading of 2 mol% after 72 h at 25 °C. Increasing the catalyst loading (4 mol%) afforded polymer **1c** of M_w 9.360 and $Đ$ of 2.57 (Table 1, entries 4–5). Raising the temperature was not effective in increasing the molecular weight of the polymer, likely due to the low boiling point of propargyl ether. Similarly, an oligomer of M_w 1.150 and $Đ$ of 3.94 was obtained in the polyhydrothiolation of **d** after 48 h at 25 °C using a 4 mol% catalyst loading. Catalyst performance improved with increasing temperature to 40 °C. The M_w of polymer **1d** increased up to 19.300 and 47.100, with $Đ$ of 1.97 and 2.07, after 24 and 48 h, respectively, using a 4 mol% catalyst at 40 °C. However, the copolymerization reaction under these conditions after 48 h also afforded a small fraction of polymer of very high molecular weight (9 %, respectively) (Table 1, entries 6–8).

The light scattering and refractive index SEC chromatograms including the MM (molar mass) *vs* elution volume plot for a representative polymer **1b** are shown in Fig. 4. Similar graphs for the polymers prepared in Tables 1 and 2 and the root mean square radius of selected polymers of high weight-average molar mass can be found in the Supplementary Material.

Polyhydrothiolation reactions with the flexible dithiol 2,2′-(ethylendioxy)diethanethiol (**2**) (Scheme 1) proceeded efficiently with rigid aromatic dialkynes. The copolymerization of **2** with **a** in the presence of 1 mol% of catalyst RhCl(IPr)(py)(η^2-coe) for 48 h at 25 °C afforded polymer **2a** with M_w of 69.900 and a narrow $Đ$ of 1.60. Increasing the catalyst loading to 2 mol% under the same reaction conditions resulted in a higher M_w polymer with a broader polydispersity, M_w of 112.000 and $Đ$ of 2.59. A further increase of the catalyst loading gave a polymer

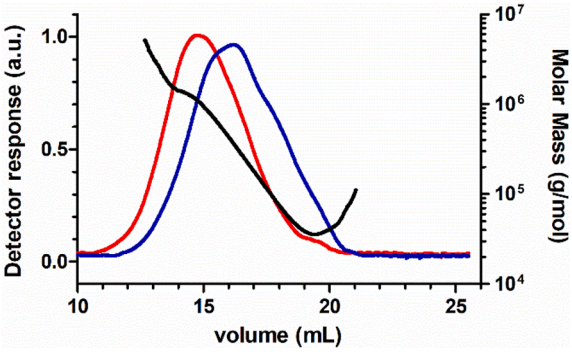


Fig. 4. a) Light scattering (blue) and refractive index (red) chromatograms, and MM (black) *vs* elution volume (mL) plot for polymer **1b** prepared at 25 °C with 1 mol% of rhodium catalyst for 48 h (Table 1, entry 3).

with a bimodal SEC profile consisting of two fractions, M_w 27.000 (44 %) and M_w 173.000 (56%) with $Đ$ of 1.59 and 1.30, respectively (Table 2, entries 1–3). The cumulative weight fraction *vs* molar mass plots for polymer **2a** prepared at 25 °C for 48 h with catalyst loadings of 1, 2 and 3 mol% are shown in Fig. 5.

The click polymerization reaction of **2** with **b** at 25 °C for 48 h using a 1 mol% of catalyst, gave a polymer **2b** with an M_w of 46.400 and $Đ$ of 2.84. The evolution of the molar mass of the polymer **2b** with increasing catalyst loading under these conditions is presented in Fig. 6, in which the cumulative molar mass distribution plots are shown. As can be seen in Table 2, the initial decrease in M_w to 27.500 at 2 mol% catalyst loading is followed by an increase of M_w reaching 124.000 at 4 mol% (Table 2, entries 4–7). Finally, the catalyst was found to be inefficient in the copolymerization of **2** with **d** affording **2d** oligomers of M_w around 4.000 even when the reaction was carried out at 50 °C (Table 2, entries 8–9).

Polyhydrothiolation reactions with the rigid dithiol 4,4′-thiobisbenzenethiol (**3**) (Scheme 1) proceeded slowly at room temperature and therefore more forcing conditions were required. The reaction involving dithiol **3** and **a** using 2 mol% of catalyst RhCl(IPr)(py)(η^2-coe) for 48 h at 25 °C afforded a low molecular weight polymer **3a** of M_w 10.000. Gratifyingly, at 50 °C under the same reaction conditions, a polymer of M_w 117.000 was obtained albeit with a broad polydispersity (Table 2, entries 10–11). Unfortunately, the copolymerization of dithiol **3** and **b** directly produce an insoluble orange solid that could not be characterized. However, copolymerization of **3** with **d** at 50 °C for 48 h using a 2 mol% catalyst load afforded polymer **3d** with a M_w of 139.000 and a $Đ$ of 2.63. Increasing the catalyst load to 3 mol% under the same reaction conditions gave a polymer **3d** that exhibited a bimodal molecular weight distribution with a light fraction (M_w = 97.000, 28%) and a main fraction of very high molecular weight (M_w = 259.000, 72%) with a narrow polydispersity index of 1.51 (Table 2, entries 12–13).

The results described above show that polyhydrothiolation reactions by catalyst RhCl(IPr)(py)(η^2-coe) provide access to high molecular weight polymers when rigid building blocks, dithiols and/or dialkynes, are involved in the copolymerization reaction. In contrast, the combination of flexible partners resulted in the formation of oligomers in the

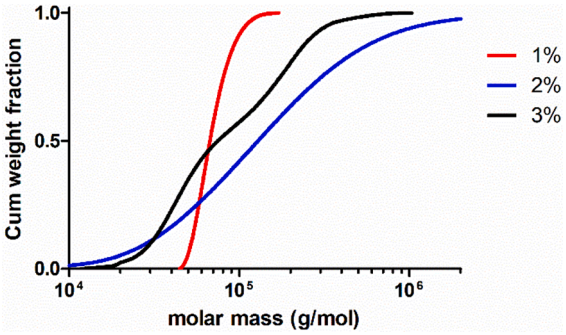


Fig. 5. Cumulative molar mass distribution plots for polymer **2a** prepared at 25 °C for 48 h with catalyst loadings of 1 mol% (red line), 2 mol% (blue line) and 3 mol% (black line) (Table 2, entries 1–3).

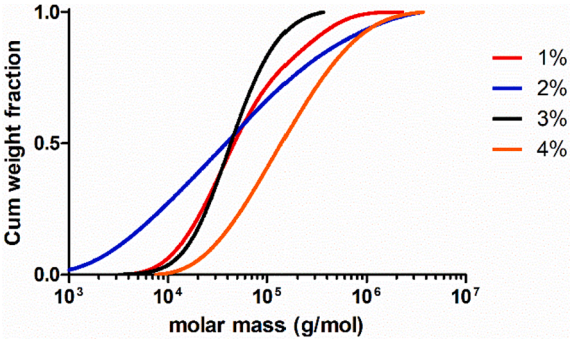


Fig. 6. Cumulative molar mass distribution plots for polymer **2b** prepared at 25 °C for 48 h with catalyst loadings of 1 mol% (red line), 2 mol% (blue line), 3 mol% (black line) and 4 mol% (orange line) (Table 2, entries 4–7).

Table 2
Click polymerization of 2,2′-(ethylendioxy)diethanethiol (**2**) and 4,4′-thiobisbenzenethiol (**3**) with dialkynes (**a**, **b** and **d**) catalyzed by [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$/py.[a]

Entry	Polymer	mol% Rh[b]	T (°C)	t (h)	M_w[c]	$Đ$ [c]	%[d]	α/β-E[e]	Yield (%)[f]
1	**2a**	1	25	48	69.900	1.60			
2	**2a**	2	25	48	112.000	2.59			
3	**2a**	3	25	48	173.000	1.59	56	6.5	86
					27.000	1.30	44		
4	**2b**	1	25	48	46.400	2.84			
5	**2b**	2	25	48	27.500	4.03			
6	**2b**	3	25	48	41.500	2.10		4.0	95
7	**2b**	4	25	48	124.000	3.42			
8	**2d**	3	25	48	4.340	5.58		1.4	43
9	**2d**	2	50	48	4.130	2.00			
10	**3a**	2	25	48	10.000	2.65			
11	**3a**	2	50	48	117.000	6.98		4.1	99
12	**3d**	2	50	48	139.000	2.63			
13	**3d**	3	50	48	259.000	1.51	72	3.0	97
					97.000	1.18	28		

[a] Reactions carried out in THF, [dithiol] = [dialkyne] = 0.157 M. [b] mol% of catalyst RhCl(IPr)(py)(η^2-coe) formed in situ, [Rh] = 3.15–6.30 mM. [c] Estimated by SEC-MALS in THF, M_w = weight-average molecular weight, $Đ$ = dispersity (M_w/M_n, M_n = number-average molecular weight). [d] Bimodal distribution, weight percentage of each fraction. [e] Ratio between vinylidene (α) and *E*-vinylene (β-*E*) groups determined by ^{1}H NMR. [g] Isolated yield.

case of **2d** even increasing the catalyst loading and/or temperature. The likely formation of entangled oligomers, which hinder the access of the reactive ends to the catalyst, may explain the lack of reactivity in this case.

2.3. Poly(vinylidene sulfide)s characterization

Conventional methods for isolating polymers from freshly prepared solutions resulted in intractable grayish-white rubbery materials. Therefore, an alternative methodology was applied. The polymer solutions in THF were brought to dryness under vacuum to give brown-orange residues, which were dried under vacuum for 48 h. The addition of anhydrous THF gave rise to yellow-orange gels of plastic appearance with different morphologies depending on the polymer (Fig. 7). These gels were washed with THF and dried under vacuum for 48 h to remove the solvent entrapped in the polymer. In this way, the polymers were obtained as orange-brown solids with fibrillar or laminar morphology, with moderate to good yields (Tables 1 and 2). Polymers **3a** and **3d** were isolated by precipitation with *n*-hexane, resulting in the formation of oily residues that were transformed into orange-brown solids of plastic texture after prolonged agitation. Field-emission scanning electron microscopy (FE-SEM) measurements of selected polymers evidenced that the fibrillar network is composed of rolled-sheets (see Supplementary Material). In addition, energy dispersive X-ray spectroscopy (EDX) analysis showed the absence of rhodium, suggesting that the catalyst was completely removed from the polymer samples by the established procedure.

The obtained polymers are sparingly soluble in most organic solvents and their characterization by NMR was carried out directly from the reaction mixture. At the end of the polymerization experiments, aliquots (0.1 mL) were taken under argon atmosphere and transferred to an NMR tube. The solvent was removed under vacuum, and the residue dissolved in $CDCl_3$ to record the ^1H and $^{13}C\{^1H\}$ NMR spectra. The NMR spectra of polymers do not show any of the characteristic resonances of the monomers, neither the -SH resonance of the dithiols nor the ≡CH resonance of the dialkynes. In fact, the monomers disappear a few hours after the start of the reaction to give oligomeric fragments that react with each other to form the polymeric chains. The stretching vibrations of ≡C–H and S–H in the monomers were observed in the range 3305–3295 and 2570–2555 cm^{-1}, respectively. These characteristic absorptions, however, disappeared in the spectra of the polymers, indicating that both functional groups have reacted in the polymerization reaction. As confirmed by NMR, the polymers have a structure mainly based on vinylidene moieties alternating with vinylene groups that derives from the regioselectivity imparted by the Rh(I)–NHC catalyst in the hydrothiolation reaction.

The most informative part of the ^1H NMR spectra is the vinyl region which shows the characteristic resonances of the vinylidene (>C=CH_2) and vinylene (–CH=CH–) groups. As an example, the ^1H NMR spectrum of **2b** shows two well separated set of resonances between δ 5.5 and 5.1 ppm that correspond to the *exo*-methylene protons (=CH_2) of the vinylidene groups. The more intense resonances at δ 5.48 and 5.25 ppm were assigned to α-α-α sequences, whereas the remaining four resonances correspond to α-β-α sequences. The = CH resonances of the vinylene groups were observed around δ 6.6 ppm as AB quartets with J_{AB} coupling constants of 12–16 Hz, which agrees with an *E* configuration (Fig. 8). The $^{13}C\{^1H\}$ NMR spectrum of **2b** was interpreted with the help of the two-dimensional ^1H–^{13}C HSQC correlation spectrum. The quaternary carbon atoms of the vinylidene groups were observed at δ 144 ppm while the =CH_2 appeared around 112 ppm. The carbon atoms of the vinylidene groups were observed above 125 ppm.

The integration of the *exo*-methylene protons (=CH_2) of the vinylidene groups and the = CH resonances of the vinylene groups in the ^1H NMR spectra allowed us to calculate the vinylidene content in the polymers (Tables 1 and 2). The α/β-*E* ratio for polymers **1a** and **1b** were 3.3 and 4.0, respectively, which was slightly lower than that found in the hydrothiolation of phenylacetylene with **1** as model reaction (7.3) that gave the divinyl sulfide products: α-α (88%) and α-β-*E* (12%). On the other hand, the hydrothiolation of phenylacetylene with **2** gave the divinyl sulfide products, α-α (83%) and α-β-*E* (17%), in a ratio of 4.9, in the order of those found for polymers **2a** and **2b**, which were 6.5 and 4.0, respectively. Finally, the α/β-*E* ratio of 4.1 for polymer **3a** is close to the value of 4.6 found in the hydrothiolation of phenylacetylene with **3** (see the Experimental Section).

Isolation of selected polymers in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT) did not affect their morphology which excludes free radical-induced cross-linking of the polymer chains. In fact, the FTIR-ATR spectra of the polymers showed two absorptions at around 1675 (s) and 1590 (m) cm^{-1}, which are associated with C=C stretching vibration of the vinylidene and vinylene groups, respectively [43].

The thermal properties of polymers have been studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Table 3). Polymers **1a** and **1d** are thermally stable up to 200 °C, which is in contrasts to the low thermal stability of **1b** and **1c** (Fig. 9). Polymers **1a**-**1d** exhibited degradation temperatures corresponding to weight losses of 5%, in the range 190–300 °C ($T_{5\%}$). Considering the onset

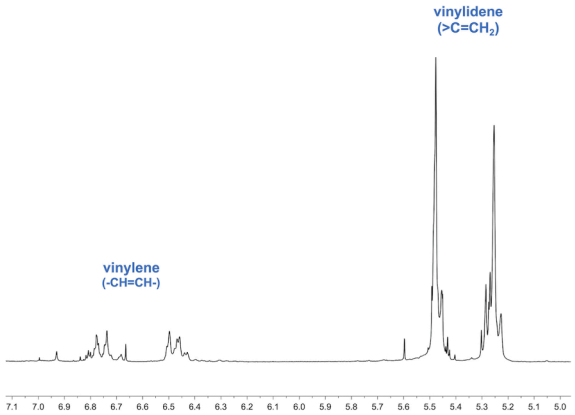


Fig. 8. Vinyl region of the ^1H NMR spectrum of polymer **2b** in $CDCl_3$.

Fig. 7. Representative photographs of polymers **2a** (left) and **2b** (right) in THF.

Table 3
Thermal properties of the poly(vinylidene sulfide)s derived from TGA, DTGA and DSC.

Polymer	$T_{5\%}$ (°C) [a]	R_w (%) [b]	T_{on} (°C)[c]	T_{max} (°C) [d]	Other (°C) [e]	Exothermic process (°C)
1a	288	30	300	322	402	137
1b	206	23	266	299	165,[f] 400	154
1c	193	18	227	295	458	> 180
1d	294	11	317	342	366	133
2a	254	10	265	292	420	127, 180
2b	253	34	280	305	83,[f] 398	133
2d	235	3	261	299	347, 392, 460	145, 192
3a	197	43	302	330	133,[f] 270,[f] 458, 561	150
3d	281	31	280	307	443, 498	153, 205

[a] Temperature at 5% weight loss; [b] R_w = Residual weight at 800 °C; [c] T_{on} = onset temperature for the degradation stage with maximum mass loss. [d] T_{max} = temperature of the maximum weight loss rate. [e] Other maxima in the derivative thermogravimetric curve. [f] Loss of solvent (THF).

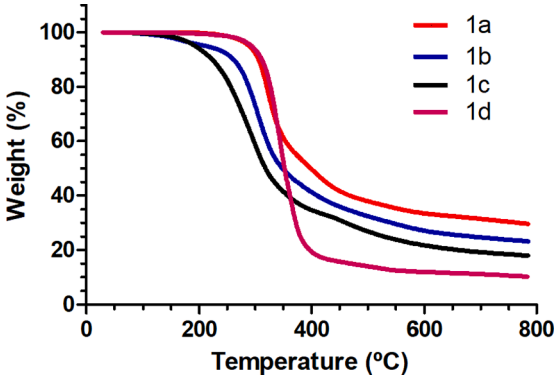


Fig. 9. TGA thermograms of polymers **1a**, **1b**, **1c** and **1d**.

temperature for the degradation stage with the maximum mass loss rate (T_{on}), oligomer **1c** is the least stable in this series, with **1d** being the most stable. According to derivative thermogravimetric (DTGA) curves, the samples showed two well-defined stages of degradation with temperatures of the maximum weight loss rate (T_{max}) in the range 227–317 °C. Polymer **1b** exhibited an additional peak at 165 °C which is ascribed to the loss of occluded solvent (THF). All four polymers thermally degrade at 800 °C producing residues of 10–30% by weight. The thermal properties of **2a** and **2b** closely resembles those of the previous described polymers with **2b** being the most stable in this series. In sharp contrast, oligomer **2d** showed four well-defined stages of degradation in the DTGA curve with temperatures of the maximum weight loss rate (T_{max}) in the range 299–460 °C and a very low residual mass at 800 °C. Finally, polymers **3a** and **3b** showed comparable stabilities to the related polymers prepared with the same dialkyne, with **3a** being slightly more stable. However, both polymers showed three well-defined stages of degradation in the DTGA curves with temperatures of the maximum weight loss rate (T_{max}) of 330 and 307 °C, respectively. The two peaks at temperatures below T_{on}, 302 °C, in the derivative thermogravimetric (DTGA) curve of **3a** are attributed to the presence of occluded THF, which was no removed by the standard protocol applied.

The DSC thermograms of most polymers recorded during the first heating cycle exhibited a rather broad exothermic peak in the range 130–180 °C that was not detected in subsequent scans (see Supplementary Material). However, polymers **2a**, **2d** and **3d** showed two peaks that were also undetected in subsequent scans. These peaks were ascribed to thermally induced olefin polymerization leading to cross-linking of polymer chains [23,27].

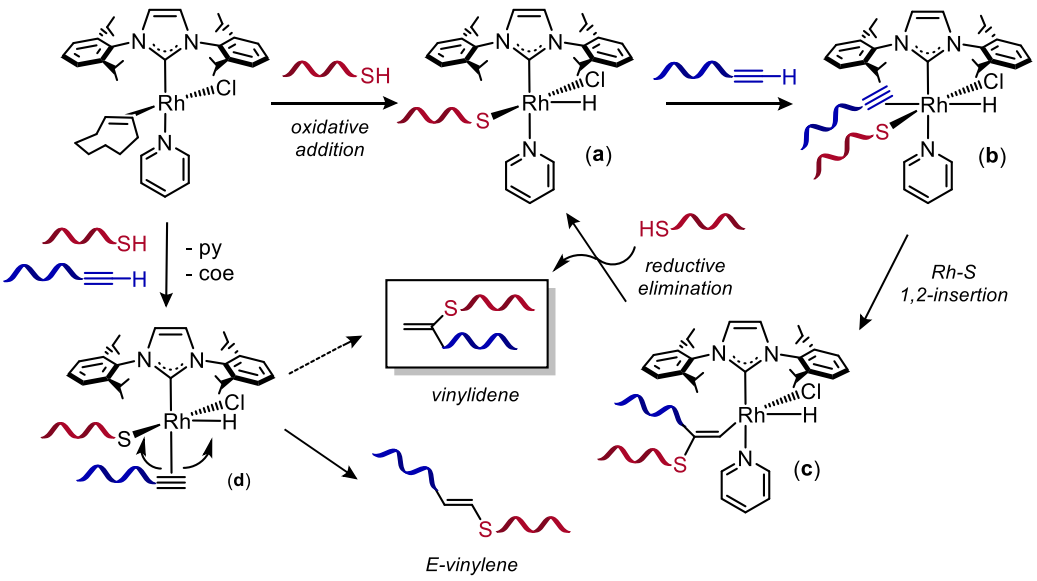
2.4. Mechanistic considerations

A mechanistic proposal that account for the high vinylidene content in the polymers is shown in Scheme 2 in which polymers with -SH and alkyne endings are depicted. This proposal is based on previous studies on the hydrothiolation of alkynes with thiols which support a classical mechanism starting with oxidative S-H addition and successive alkyne insertion and reductive elimination processes [38]. Catalyst RhCl(IPr)(py)(η^2-coe) reacts with a thiol fragment by S-H oxidative addition to afford an unsaturated Rh^{III} hydride thiolate specie (**a**). Coordination of an alkyne moiety to afford (**b**) followed by 1,2-insertion of the alkyne into the Rh-S bond results in the branched alkenyl-Rh^{III}-hydride intermediate (**c**). Reductive elimination of the branched vinyl sulfide followed by reaction with a new thiol fragment affords the catalytic active species (**a**). In this regard, it is worth mentioning that catalyst RhCl(IPr)(py)(η^2-coe) reacts with Ph-SH to afford the square-pyramidal compound RhClH(SPh)(IPr)(py), similar to **a** in Scheme 2. This unsaturated species further reacted with phenylacetylene to afford the branched phenyl(1-phenylvinyl)sulfane product, resulting from the Markovnikov addition of Ph-SH to the alkyne [38].

The stereochemistry of the square-pyramidal hydride species (**a**) is key to explaining the observed regioselectivity outcome. The high trans influence of the hydride ligand directs the coordination of the alkyne fragment *cis* with respect to the thiolate fragment thus promoting the insertion of the alkyne into the Rh-S bond, which leads to the branched vinylidene sulfide. This ligand arrangement also prevents the alkyne insertion into the Rh-H bond, which would result in the linear *E*-vinylene sulfide. The coordination of pyridine to the Rh(I) center is crucial for the regioselectivity. In fact, decoordination of pyridine give rise to a hypothetical square-pyramidal species (**d**) with the alkyne ligand *cis* to both hydride and thiolate ligand in which Rh-H insertion is favored. Thus, a moderated excess of pyridine is required to increase the concentration of (**a**) in the reaction medium. However, since pyridine and alkyne can compete for the coordination vacancy of (**a**), a large excess of pyridine would hinder alkyne coordination, leading to a decrease in catalytic activity.

3. Conclusions

The system [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$/pyridine efficiently catalyzed the thiol-yne click polymerization of a series of dithiols and dialkynes, yielding sulfur-rich vinylidene-based polymers with vinylidene content of 75–87% using catalyst loadings of 1–4 % and mild reaction conditions. The poly(vinylidene sulfide)s were characterized by SEC-MALS, FTIR-ATR and NMR, which allowed the vinylidene content and the molecular weight of the polymers to be evaluated. The properties of the polymers were found to be greatly influenced by the structure of the monomers and their interaction with the catalyst. High molecular weight polymers were obtained in the copolymerization of flexible dithiols, such as 1,6-hexanedithiol (M_w up to 199.000) and 2,2′-(ethylendioxy)diethanethiol (M_w up to 173.000), with rigid aromatic dialkynes, namely 1,4-diethynylbenzene and 1,3-diethynylbenzene, respectively, at low catalyst loading under mild conditions. Also, polyhydrothiolation of the rigid dithiol 4,4′-thiobisbenzenethiol with the flexible 1,7-octadiyne gave a polymer with a bimodal molecular weight distribution with a main fraction of very high molecular weight (M_w up to 259.000). In contrast, polyhidrothiolation of flexible dialkynes, such as 1,7-octadiyne, with flexible dithiols was much less efficient and resulted in the formation of oligomers, although increasing the temperature allowed to prepare polymers in some cases. The formation of poly(vinylidene sulfide)s is consequence of the synergistic effect of the IPr and pyridine ligands on the RhCl(IPr)(py)(η^2-coe) catalyst, which controls the regioselectivity of the alkyne insertion step towards the branched vinyl sulfide.



Scheme 2. Proposed catalytic cycle for the thiol-yne click polymerization of dialkynes with dithiols.

4. Experimental Section

4.1. General procedure and materials

All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Solvents were obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ [44] was prepared according to the literature procedure. Pyridine (ρ = 0.978 g mL^{-1}, 99%) and the monomers: 1,6-hexanedithiol (ρ = 0.983 g mL^{-1}, 97%), 2,2′-(ethylendioxy)diethanethiol (ρ = 1.120 g mL^{-1}, 95%), 4,4′-thiobisbenzenethiol (98%), 1,3-diethynylbenzene (ρ = 0.949 g mL^{-1}, 97%), 1,4-diethynylbenzene (95%), propargyl ether (ρ = 0.914 g mL^{-1}, 98%) and 1,7-octadiyne (ρ = 0.800 g mL^{-1}, 98%), were purchased from Merck and used as received.

4.2. Scientific equipment

The absolute molecular weight averages (M_n and M_w), dispersity ($Đ$, M_w/M_n) and molecular weight distribution were determined by SEC-MALS at the Chromatography and Spectroscopy Service of the ISQCH. SEC-MALS analyses were carried out using a Waters 2695 instrument equipped with two Phenogel linear (2) (30 × 7.8 mm, 5 μm) columns fitted to a MALS detector (MiniDawn Treos, Wyatt) and a differential refractive index detector (Optilab Rex, Wyatt). The polymer solutions in THF (≈ 2.0 mg/mL) were filtered through a 0.45 μm PTFE membrane filter before being injected in the GPC systems. Data analysis was performed with ASTRA Software from Wyatt. Polymer samples were eluted at 35 °C with THF at a flow rate of 1.0 mL/min. *dn/dc* values in THF were determined at 658 nm using the full mass recovery method, in which it is assumed the recovery of 100% of the injected mass of a polymer sample of known concentration [45]. Accurately weighted sample of polymer (2.0 mg mL^{-1}) were dissolved in the minimum amount of chloroform to yield a clear solution (around 0.1 mL) then the solution was taken to the required volume with THF. Thus, *dn/dc* values of **1a**, **1b**, **1c**, **1d**, **2a**, **2b**, **2d**, **3a** and **3d** were determined to be 0.158, 0.158, 0.141, 0.136, 0.139, 0.143, 0.131, 0.289 and 0.221 mL/g, respectively.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AV-400 (400.16 MHz) and AV-300 (300.13 MHz) spectrometers. Chemical shifts are reported in ppm relative to tetramethylsilane and referenced to partially deuterated solvent resonances. Coupling constants (*J*) are given in Hertz. Spectral assignments were achieved by combination of ^{1}H–^{1}H COSY, ^{13}C DEPT and APT, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC experiments. Infrared spectra were recorded on a FT-IR Perkin-Elmer Spectrum 100 Spectrophotometer equipped with a Universal Attenuated Total Reflectance (UATR) accessory made by thallium bromide-iodide crystals (KRS-5), which allows the observation of the electromagnetic spectrum over the 4000–250 cm^{-1} region. Thermal gravimetric analyses were carried out on a TA Q-5000 TGA apparatus (TA Instruments). Samples were heated under nitrogen from room temperature to 800 °C at a rate of 10 °C/min. Differential scanning calorimetry experiments were carried out on a DSC Q-20 apparatus (TA Instruments). Samples were heated under nitrogen from 20 °C to 160/220 °C at a rate of 10 °C/min and cooled to the initial temperature at the same rate. In some experiments this cycle was repeated several times. Field emission scanning electron microscopy (FE-SEM) images were recorded using Carl Zeiss MERLIN scanning electron microscope at the Microscopy Service Laboratory of the University of Zaragoza. The polymer samples were fixed onto glass and coated with gold.

4.3. Preparation of model compounds for poly(vinylidene sulfide)s polymers

*Hydrothiolation of phenylacetylene with 1,6-hexanedithiol (**1**).* A solution of [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (6.4 mg, 5 μmol) in C_6D_6 (0.5 mL, NMR tube) was treated with pyridine (4.1 μL, 0.05 mmol), 1,6-hexanedithiol (**2**) (78.8 μL, 0.5 mmol) and phenylacetylene (112.1 μL, 1.0 mmol) at room temperature. ^{1}H NMR after 0.7 h showed the complete conversion of the reactants to a mixture of divinysulfides: α-α (88%), α-β-*E* (12%) and β-*E*-β-*E* (traces). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.72 (dd, J_{H-H} = 8.1, J_{H-H} = 1.2, 4H, $H_{o\text{-}Ph}$), 7.3–7.1 (br, 6H, Ph), 5.51 and 5.24 (both s, 4H, =CH_2), 2.54 (t, J_{H-H} = 7.4, 4H, S-CH_2), 1.50 (m, 4H, –CH_2), 1.17 (m, 4H, CH_2) (α-α); δ 6.66 (ABq, J_{AB} = 15.0, 2H, =CH), 5.51 and 5.25 (both s, 2H, =CH_2) (α-β); δ 6.67 (ABq, J_{AB} = 15.0, 4H, =CH) (β-β). ^{13}C{^{1}H} NMR (75.46 MHz, C_6D_6, 298 K): δ 145.8 (*C* = CH_2), 140.1 ($C_{q\text{-}Ph}$), 128.7 ($C_{p\text{-}Ph}$), 128.4 ($C_{m\text{-}Ph}$), 127.3 ($C_{o\text{-}Ph}$), 110.3 (C = *C*H_2), 31.9 (S-CH_2), 28.4 (CH_2), 28.3 (CH_2) (α-α); δ 126.8, 125.7 (=CH), 32.26 (S-CH_2), 29.23 (CH_2), 28.23 (CH_2) (α-β-*E*); δ 126.7, 125.6 (=CH) (β-*E*-β-*E*).

*Hydrothiolation of phenylacetylene with 2,2′-(ethylenedioxy)diethanethiol (**2**).* A solution of [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (6.4 mg, 5 μmol) in C_6D_6 (0.5 mL, NMR tube) was treated with pyridine (4.1 μL, 0.05 mmol), 2,2′-(ethylendioxy)diethanethiol (**2**) (85.7 μL, 0.5 mmol) and phenylacetylene (112.1 μL, 1.0 mmol) at room temperature. ^{1}H NMR after 1 h showed complete conversion of the reactants to a mixture of

divinysulfides: α-α (83%) and α-β-*E* (17%). ^{1}H NMR (400.16 MHz, C_6D_6, 298 K): δ 7.53 (dd, $J_{H\text{-}H}$ = 8.2, 1.4, 4H, $H_{o\text{-}Ph}$), 7.10, (dd, $J_{H\text{-}H}$ = 8.2, 7.5, 4H, $H_{m\text{-}Ph}$), 7.07 (tt, $J_{H\text{-}H}$ = 7.5, 1.4, 2H, $H_{p\text{-}Ph}$), 5.33 and 5.14 (both s, 4H, =CH_2), 3.43 (t, $J_{H\text{-}H}$ = 6.8, 4H, O-CH_2), 3.27 (s, 4H, O-CH_2CH_2), 2.71 (t, $J_{H\text{-}H}$ = 6.8, 4H, S-CH_2) (α-α); δ 7.6–7.0 (set of m, 10*H*, H_{Ph}), 6.55 (ABq, J_{AB} = 15.5, 2H, =CH), 5.35 and 5.15 (both s, 2H, =CH_2), 3.44 (t, $J_{H\text{-}H}$ = 6.6, 4H, O-CH_2), 3.29 (s, 4H, O-CH_2CH_2O), 2.70 (t, $J_{H\text{-}H}$ = 6.6, 4H, S-CH_2) (α-β-*E*). ^{13}C{^{1}H} (75.46 MHz, C_6D_6, 298 K): δ 145.4 (*C* = CH_2), 140.0 ($C_{q\text{-}Ph}$), 128.7 ($C_{p\text{-}Ph}$), 128.7 ($C_{m\text{-}Ph}$), 127.6 ($C_{o\text{-}Ph}$), 111.1 (s, C = *C*H_2), 70.6 (-O-CH_2CH_2O), 69.7 (O-CH_2), 32.0 (S-CH_2) (α-α); δ 145.3 (s, *C* = CH_2), 137.5 ($C_{q\text{-}Ph}$), 128.9 ($C_{m\text{-}Ph}$), 127.4 ($C_{p\text{-}Ph}$), 127.1 and 126.0 (=CH), 125.9 ($C_{o\text{-}Ph}$), 111.0 (C = *C*H_2), 70.8 (O-CH_2CH_2-O), 70.7 (O-CH_2), 32.6 (S-CH_2) (α-β-*E*).

*Hydrothiolation of phenylacetylene with 4,4′-thiobisbenzenethiol (**3**).* A solution of [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (6.4 mg, 5 μmol) in C_6D_6 (0.5 mL, NMR tube) was treated with pyridine (4.1 μL, 0.05 mmol), 4,4′-thiobisbenzenethiol (**3**) (127,8 mg, 0.5 mmol) and phenylacetylene (112.1 μL, 1.0 mmol) at room temperature. ^{1}H NMR after 24 h showed complete conversion of the reactants to a mixture of divinysulfides: α-α (82%) and α-β-*E* (18%). ^{1}H NMR (400.16 MHz, C_6D_6, 298 K): δ 7.55 (dd, $J_{H\text{-}H}$ = 8.3, 1.6, 4H, $H_{o\text{-}Ph}$), 7.03 (dd, $J_{H\text{-}H}$ = 8.3, 7.6, 4H, $H_{m\text{-}Ph}$), 7.00 (td, $J_{H\text{-}H}$ = 7.6, 1.6, 2H, $H_{p\text{-}Ph}$), 7.10 and 6.92 (both d, $J_{H\text{-}H}$ = 8.5, 8H, S-C_6H_4), 5.51 and 5.33 (both s, 4H, =CH_2) (α-α); 7.71 (d, $J_{H\text{-}H}$ = 8.1, 4H, $H_{o\text{-}Ph}$), 7.15 (dd, $J_{H\text{-}H}$ = 6.9, 4H, $H_{m\text{-}Ph}$), 7.03 (t, $J_{H\text{-}H}$ = 6.9, 2H, $H_{p\text{-}Ph}$), 7.2–6.9 (set of m, 8H, S-C_6H_4), 7.04 and 6.80 (both d, $J_{H\text{-}H}$ = 14.0, 2H, =CH), 5.52 and 5.35 (both d, $J_{H\text{-}H}$ = 4.4, 2H, =CH_2) (α-β-*E*). ^{13}C{^{1}H} (75.46 MHz, C_6D_6, 298 K): δ 144.3 (*C* = CH_2), 138.9 ($C_{q\text{-}Ph}$), 135.0 and 133.8 ($C_{q\text{-}PhS}$), 132.5 and 131.7 (S-C_6H_4), 128.9 ($C_{p\text{-}Ph}$), 128.7 (s, $C_{m\text{-}Ph}$), 127.6 (s, $C_{o\text{-}Ph}$), 117.3 (C = *C*H_2) (α-α); 144.1 (s, *C* = CH_2), 138.8 ($C_{q\text{-}Ph}$), 136.7 and 134.2 ($C_{q\text{-}PhS}$), 132.4, 132.3, 132.2, 132.1, 131.5, 131.4, 129.0, 128.8, 128.6, and 126.5 (C_{Ph}), 126.6 and 122.8 (=CH), 117.6 (s, C = *C*H_2) (α-β-*E*).

4.4. Polymer synthesis and characterization

General Procedure. [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (3.1–12.6 μmol) was weighed in a Schlenk tube (25 mL) inside a glovebox. The catalyst was dissolved in degassed THF (2.5 or 4 mL) and pyridine (31–126 μmol) was added under an argon stream to give a yellow solution which was stirred for 5 min. Then, the dithiol (0.628 mmol) and diyne (0.628 mmol) were sequentially added under an argon stream to give red–orange solutions which were stirred for the appropriate reaction time at the selected temperature. The resulting orange-brown solutions were brought to dryness under vacuum to give oily residues which were dried under vacuum for 36–72 h. The dark orange-brown residues were washed with THF (3 mL) to give the polymers as jelly-like solids in most cases, which were filtered under argon using cannula techniques, washed with THF (2 × 2 mL) and dried under vacuum for 48 h.

Polymers **3a** and **3d** were isolated by precipitation with *n*-hexane. The resultant solutions from the polymerization reactions were added dropwise into 40 mL of *n*-hexane through a cannula under stirring to give immediately oily suspensions which were further stirred for 24 h. The suspensions were decanted to give orange-brown solids with plastic aspect which were washed with *n*-hexane and dried under vacuum for 48 h.

Monitoring of the polymerization reactions. The polymerization reactions were monitored by ^{1}H NMR spectroscopy. Aliquots (0.1 mL) were taken from the reaction mixture at different reaction times and transferred to an NMR tube under argon.[‡] The solvent was removed under vacuum and the residue dissolved in $CDCl_3$. The poor solubility of some isolated polymers in THF precludes the determination of the polymer molecular weight in this solvent after isolation, therefore SEC-MALS analysis was carried on aliquots (0.1 mL) of freshly made THF solutions of the polymers, after quenching with MeOH (0.1 mL), which were diluted to 2.0 mg/mL before analyses [46–47].

*Synthesis and characterization of polymer **1a**.* [[Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (8.0 mg, 6.3 μmol), pyridine (5.1 μL, 0.063 mmol), 1,6-hexanedithiol (**1**) (99.0 μL, 0.628 mmol) and 1,3-diethynylbenzene (**a**) (86.0 μL, 0.628 mmol) in THF (2.5 mL) at room temperature for 24 h. Yield: 73 mg (42 %), orange needles. Bimodal distribution: M_w = 42.000, $Đ$ = 1.78 (80 %); M_w = 4.700, $Đ$ = 1.11 (20 %). ^{1}H NMR (400.16 MHz, $CDCl_3$, 298 K): δ 7.71 (m), 7.49 (dd, $J_{H\text{-}H}$ = 15.8 and 7.8), 7.44 (m), 7.31 (m), 7.14 (m) (Ph), 6.60 (ABq, J_{AB} = 12.0), 6.57 (ABq, J_{AB} = 12.0) (=CH *trans*), 5.47, 5.44, 5.16, 5.14 (=CH_2), 2.79, 2.67 (m, S-CH_2), 1.63, 1.40 (m, >CH_2). α/β-*E* ratio = 4.0. ^{13}C{^{1}H} (100.62 MHz, C_6D_6, 298 K): δ 145.2, 145.0 (*C*=CH_2), 140.3, 140.0, 137.3 (C_q, Ph), 128.7, 128.5, 127.2 (Ph), 126.3, 126.0 (=CH *trans*), 125.9 (Ph), 125.7, 125.5 (=CH *trans*), 124.3 (Ph), 110.8, 110.7, 110.5 (C=*C*H_2), 32.5, 32.1, 29.31, 28.5, 28.4 (>CH_2). IR (ATR, cm^{-1}): ν(C=C), 1679 (s), 1594 (m).

*Synthesis and characterization of polymer **1b**.* [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (4.0 mg, 3.1 μmol), pyridine (2.6 μL, 0.031 mmol), 1,6-hexanedithiol (**1**) (99.0 μL, 0.628 mmol) and 1,4-diethynylbenzene (**b**) (83.4 mg, 0.628 mmol) in THF (2.5 mL) at room temperature for 24 h. Yield: 123 mg (71 %), orange-brown plates and needles. M_w = 46.900, $Đ$ = 1.85. ^{1}H NMR (400.16 MHz, $CDCl_3$, 298 K): δ 7.52 (s), 7.34 (ABq, J_{AB} = 12.0) (Ph), 6.59 (ABq, J_{AB} = 16.0), 6.58 (ABq, J_{AB} = 16.0), 6.55 (ABq, J_{AB} = 14.0) (=CH *trans*), 5.48, 5.45, 5.17, 5.16, 5.14 (=CH_2), 2.80, 2.67 (m, S-CH_2), 1.63, 1.42 (m, >CH_2). α/β-*E* ratio = 4.0. ^{13}C{^{1}H} (75.46 MHz, C_6D_6, 298 K): δ 144.8, 144.7, 144.3 (*C*=CH_2), 140.2, 139.9, 138.1, 137.6, 137.4 (C_q, Ph), 132.6, 132.2, 127.5, 127.2 (Ph), 126.2, 126.0, 125.8, 125.6, 125.5, 125.3 (=CH *trans*), 111.7, 111.6, 110.8, 110.7, 110.4 (C=*C*H_2), 39.1, 32.2, 29.1, 28.6, 28.4, 28.2, 28.1 (>CH_2). IR (ATR, cm^{-1}): ν(C=C), 1671 (s), 1586 (m).

*Synthesis and characterization data for polymer **1c**.* [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (16.0 mg, 12.6 μmol), pyridine (10.3 μL, 0.126 mmol), 1,6-hexanedithiol (**1**) (99.0 μL, 0.628 mmol) and propargyl ether (**c**) (66.0 μL, 0.628 mmol) in THF (2.5 mL) at room temperature for 48 h. Yield: 108 mg (70 %), orange needles M_w = 9.360, $Đ$ = 3.3. ^{1}H NMR (400.16 MHz, $CDCl_3$, 298 K): δ 5.89 (set of ABX_2, $J_{AB} \approx$ 15.0) (=CH *trans*), 5.35, 5.30, 5.27, 4.96, 4.91, 4.88 (=CH_2), 4.04, 4.01 (m, O-CH_2), 2.70, 2.66 (m, S-CH_2), 1.62, 1.40 (m, >CH_2). α/β-*E* ratio = 3.3. ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$, 298 K): δ 147.7 (*C*=CH_2), 129.7, 128.9, 128.8, 128,6, 123.4, 123.2, 122.9 (=CH *trans*), 109.77, 109.0, 108.5 (C=*C*H_2), 72.7, 72.6, 72.4, (O-CH_2), 31.0, 31.0, 28.7, 28.4, 28.4 (>CH_2). IR (ATR, cm^{-1}): ν(C=C), 1671 (s), 1586 (m).

*Synthesis and characterization data for polymer **1d**.* [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (16.0 mg, 12.6 μmol), pyridine (10.3 μL, 0.126 mmol), 1,6-hexanedithiol (**1**) (99.0 μL, 0.628 mmol) and 1,7-octadiyne (**d**) (85.0 μL, 0.628 mmol) in THF (2.5 mL) at 40 °C for 48 h. Yield: 106 g (66 %), orange brown solid. Bimodal distribution: M_w = 47.100, $Đ$ = 2.07 (91 %); M_w = 372.000, $Đ$ = 1.30 (9 %). ^{1}H NMR (400.16 MHz, $CDCl_3$, 298 K): δ 5.75 (set of ABX_2, $J_{AB} \approx$ 15.0, =CH *trans*), 5.03, 5.01, 5.00, 4.67, 4.66 (=CH_2), 2.79, 2.68, 2.62 (t, $J_{H\text{-}H}$ = 7.4, S-CH_2, hdt), 2.22, 2.08 (m, >CH_2, octd), 1.64 (m, >CH_2, hdt), 1.55 (m, >CH_2, octd), 1.42 (m, >CH_2, hdt) (hdt = hexanedithiol, octd = octanediyne). α/β-*E* ratio = 1.5. ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$, 298 K): δ 145.9, 145.8 (*C*=CH_2), 130.6, 123.1 (=CH *trans*), 105.5, 105.4 (C=*C*H_2), 37.7, 37.5, 37.5, 33.1, 33.1, 32.8, 31.2, 30.3, 29.5, 28.8, 28.4, 28.1 (>CH_2). IR (ATR, cm^{-1}): ν(C=C), 1709 (s), 1598 (m).

*Synthesis and characterization data for polymer **2a**.* [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (12.0 mg, 9.4 μmol), pyridine (7.7 μL, 0.094 mmol), 2,2′-(ethylendioxy)diethanethiol (**2**) (107.6 μL, 0.628 mmol) and 1,3-diethynylbenzene (**a**) (86.0 μL, 0.628 mmol) in THF (4 mL) at room temperature for 48 h. Yield: 167 mg (86 %), orange-brown plates and needles. Bimodal distribution: M_w = 173.000, $Đ$ = 1.59 (56 %); M_w = 27.000, $Đ$ = 1.30 (44 %). ^{1}H NMR (400.16 MHz, $CDCl_3$, 298 K): δ 7.69 (m), 7.53–7.45 (m), 7.43 (m), 7.35–7.21 (m) (Ph), 6.63 (ABq, J_{AB} = 16.0), 6.48 (ABq, J_{AB} = 16.0) (=CH *trans*), 5.48, 5.47, 5.44, 5.27, 5.26, 5.24 (=CH_2), 3.67–3.61 (set of m), 3.60, 3.57 (m) (O-CH_2), 2.99, 2.88, 2.69 (m, S-CH_2). α/β-*E* ratio = 6.5. ^{13}C{^{1}H} (75.46 MHz, $CDCl_3$, 298 K): δ 144.2 (*C*=CH_2), 144.1, 140.5, 139.6, 128.5, 128.4, 127.8, 127.7, 127.4 (Ph), 126.0, 125.6 (C=CH *trans*), 111.8, 111.7 (C=*C*H_2), 70.3, 70.2,

69.5, 68.0 (O-CH_2), 31.4, 31.0 (S-CH_2). IR (ATR, cm^{-1}): ν(C=C), 1671 (s), 1594 (m).

*Synthesis and characterization data for polymer **2b**.* [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (12.0 mg, 9.4 μmol), pyridine (7.7 μL, 0.094 mmol), 2,2′-(ethylendioxy)diethanethiol (**2**) (107.6 μL, 0.628 mmol) and 1,4-diethynylbenzene (**b**) (83.4 mg, 0.628 mmol) in THF (4 mL) at room temperature for 48 h. Yield: 184 mg (95 %), orange-brown plates and needles. $M_w = 41.500$, $Đ = 2.10$. ^{1}H NMR (400.16 MHz, $CDCl_3$, 298 K): δ 7.51, 7.46, 7.22 (m, Ph), 6.62 (set of ABq, $J_{AB} \approx 16.0$) (=CH *trans*), 5.48, 5.45, 5.28, 5.27, 5.25, 5.23 (=CH_2), 3.67–3.60 (set of m), 3.60, 3.57 (m) (O-CH_2), 2.99, 2.88, 2.69 (m, S-CH_2). α/β-*E* ratio = 4. ^{13}C{^{1}H} (75.46 MHz, $CDCl_3$, 298 K): δ 144.5 (*C*=CH_2), 143.7, 139.5, 132.1, 132.1, 127.5, 127.3, 127.2, 127.1 (Ph), 125.8, 125.7, 125.5, 125.3 (C=*C*H *trans*), 111.9, 111.8 (C=*C*H_2), 70.5, 70.3, 70.2, 69.5 (O-CH_2), 32.2, 31.5 (S-CH_2). IR (ATR, cm^{-1}): ν(C=C), 1671 (s), 1588 (m).

*Synthesis and characterization data for polymer **2d**.* [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (12.0 mg, 9.4 μmol), pyridine (7.7 μL, 0.094 mmol), 2,2′-(ethylendioxy)diethanethiol (**2**) (107.6 μL, 0.628 mmol) and 1,7-octadiyne (**d**) (85.0 μL, 0.628 mmol) in THF (4 mL) at room temperature for 48 h. Yield: 77.6 mg (43 %), yellow plates. $M_w = 4.340$, $Đ = 5.58$.^{1}H NMR (400.16 MHz, $CDCl_3$, 298 K): δ 5.79 (ABX_2, $J_{AB} = 14.4$, $J_{AX} < 1$), 5.78 (ABX_2, $J_{AB} = 15.1$, $J_{AX} < 1$) (=CH *trans*), 5.03, 5.02, 5.01, 4.76, 4.74, 4.73 (=CH_2), 3.70–3.55 (set of m, O-CH_2), 2.91, 2.82, 2.69 (m) (S-CH_2, hdt), 2.20, 2.07 (m, >CH_2, octd), 1.64 (m, >CH_2, hdt), 1.53 (m, >CH_2, octd), 1.38 (m, >CH_2, hdt) (hdt = hexanedithiol, octd = octanediyne). α/β-*E* ratio = 1.4. ^{13}C{^{1}H} (75.46 MHz, $CDCl_3$, 298 K): δ 144.6 (*C*=CH_2), 131.4, 131.0, 122.8, 122.5 (=CH *trans*), 106.1, 105.9, 104.4 (C=*C*H_2), 73.0, 72.9, 70.4, 70.3, 70.2, 70.1, 69.3, 68.4, 67.9 (O-CH_2), 36.8, 32.5, 32.1, 30.5 (S-CH_2), 27.8, 27.7, 27.3, 25.6, 24.3 (>CH_2). IR (ATR, cm^{-1}): ν(C=C), 1601 (s), 1534 (m).

*Synthesis and characterization data for polymer **3a**.* [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (12.0 mg, 9.4 μmol), pyridine (7.7 μL, 0.094 mmol), 4,4′-thiobisbenzenethiol (**3**) (160.4 mg, 0.628 mmol) and 1,3-diethynylbenzene (**a**) (85.01 μL, 0.628 mmol) in THF (4 mL) at 50 °C for 48 h. Yield: 224 mg (95 %), red-brown solid. $M_w = 117.00$, $Đ = 6.98$. ^{1}H NMR (400.16 MHz, $CDCl_3$, 298 K): δ 7.79 (m), 7.46 (m), 7.20 (m), 7.18 (m), 7.09 (m), 7.07 (m), (Ph), 7.10 (ABq, $J_{AB} = 8.5$) (=CH *cis*), 6.75 (ABq, $J_{AB} = 15.6$) (=CH *trans*), 5.62, 5.36 (=CH_2). α/β-*E* ratio = 4.1. IR (ATR, cm^{-1}): ν(C=C), 1677 (s), 1570 (m).

*Synthesis and characterization data for polymer **3d**.* [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (12.0 mg, 9.4 μmol), pyridine (7.7 μL, 0.094 mmol), 4,4′-thiobisbenzenethiol (**3**) (160.4 mg, 0.628 mmol) and 1,7-octadiyne (**d**) (85.01 μL, 0.628 mmol) in THF (4 mL) at 50 °C for 48 h. Yield: 218 mg (97%), brown solid. Bimodal distribution: $M_w = 25.900$, $Đ = 1.51$ (72 %); $M_w = 97.000$, $Đ = 1.18$ (28 %). ^{1}H NMR (400.16 MHz, $CDCl_3$, 298 K): 7.35–7.15 (Ph), 6.06 (set of ABq, $J_{AB} \approx 15$) (=CH *trans*), 5.19, 5.18, 5.15, 4.95, 4.91, 4.90 (=CH_2), 2.22 (m), 1.54 (m), 1.44 (m) (>CH_2). α/β-*E* ratio = 3.0. ^{13}C{^{1}H} (75.46 MHz, $CDCl_3$, 298 K): 145.3 (*C*=CH_2), 145.1, 145.0, 133.5, 133.4, 132.3, 131.5, 131.4 (Ph), 130.3, 130.1, 128.9, 128.8 (=CH *trans*), 114.1, 113.5 (C=*C*H_2), 36.2, 32.8, 28.1, 27.8, 27.5, 25.6 (>CH_2). IR (ATR, cm^{-1}): ν(C=C), 1605 (m), 1571 (m).

‡ *The underlined signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra are the more intense resonances of each type that correspond to the main sequence in the polymers.*

Data availability

Data will be made available on request.

CRediT authorship contribution statement

Pablo Hermosilla: Investigation, Methodology. **Daniel Funes-Hernando:** Investigation, Methodology. **Ricardo Castarlenas:** Funding acquisition, Conceptualization. **Andrea Di Giuseppe:** Conceptualization, Supervision, Validation. **Ramón Azpíroz:** Investigation, Validation, Writing – original draft. **Eugenio Vispe:** Investigation, Validation, Visualization. **Jesús J. Pérez-Torrente:** Funding acquisition, Conceptualization, Supervision, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Jesus J. Perez-Torrente reports financial support was provided by Spain Ministry of Science and Innovation. Jesus J. Perez-Torrente reports financial support was provided by Government of Aragón.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

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References

[1] X.-.-H. Zhang, P. Theato (Eds.), Sulfur-Containing Polymers: From Synthesis to Functional Materials, Wiley-VCH, Weinheim, Germany, 2021.
[2] H. Mutlu, E.B. Ceper, X. Li, J. Yang, W. Dong, M.M. Ozmen, P. Theato, Sulfur Chemistry in Polymer and Materials Science, Macromol. Rapid Commun. 40 (2019) 1800650.
[3] H.C. Kolb, M.G. Finn, K.B. Sharpless, Click Chemistry: Diverse Chemical Function from a Few Good Reactions, Ang. Chem. Int. Ed. 11 (2001) 2004–2021.
[4] A. Marrocchi, A. Facchetti, D. Lanari, S. Santoro, L. Vaccaro, Click-chemistry approaches to π-conjugated polymers for organic electronics applications, Chem. Sci. 7 (2016) 6298–6308.
[5] Y. Shi, J.Z. Sun, A. Qin, Click polymerization: The aurora of polymer synthetic methodology, Polym. Chem. 55 (2017) 616–621.
[6] Y. Zou, L. Zhang, L. Yang, F. Zhu, M. Ding, F. Lin, Z. Wang, Y. Li, "Click" chemistry in polymeric scaffolds: Bioactive materials for tissue engineering, J. Control Release 273 (2018) 160–179.
[7] Z. Geng, J.J. Shin, Y. Xi, C.J. Hawker, Click chemistry strategies for the accelerated synthesis of functional macromolecules, J. Polymer. Sci. 59 (2021) 963–1042.
[8] C.E. Hoyle, A.B. Lowe, C.N. Bowman, Thiol-click chemistry: a multifaceted toolbox for small molecule and polymer synthesis, Chem. Soc. Rev. 39 (2010) 1355–1387.
[9] A.B. Lowe, C.N. Bowman, Thiol-X Chemistries in Polymer and Materials Science, RSC Publishing, Cambridge, UK, 2013.
[10] J.M. Sarapas, G.N. Tew, Poly(ether–thioethers) by Thiol-Ene Click and Their Oxidized Analogues as Lithium Polymer Electrolytes, Macromolecules 49 (2016) 1154–1162.
[11] B. Alameddine, N. Baig, S. Shetty, S. Al-Mousawi, F. Al-Sagheer, Triptycene-containing Poly(vinylene sulfone) derivatives from a metal-free thiol-yne click polymerization followed by a mild oxidation reaction, Polymer 154 (2018) 233–240.
[12] N. Baig, S. Shetty, M.S. Moustafa, S. Al-Mousawi, B. Alameddine, Selective removal of toxic organic dyes using Tröger base-containing sulfone copolymers made from a metal-free thiol-yne click reaction followed by oxidation, RSC Adv. 11 (2021) 21170–21178.
[13] J.V. Burykina, A.D. Kobelev, N.S. Shlapakov, A.Y. Kostyukovich, A. N. Fakhrutdinov, B. König, V.P. Ananikov, Intermolecular Photocatalytic Chemo-, Stereo- and Regioselective Thiol–Yne–Ene Coupling Reaction, Angew. Chem. Int. Ed. 61 (2022) e202116888.
[14] R. Hoogenboom, Thiol-Yne Chemistry: A Powerful Tool for Creating Highly Functional Materials, Angew. Chem. Int. Ed. 49 (2010) 3415–3417.
[15] A.B. Lowe, C.E. Hoyle, C.N. Bowman, Thiol-yne click chemistry: A powerful and versatile methodology for materials synthesis, J. Mater. Chem. 20 (2010) 4745–4750.
[16] J.C. Worch, A.P. Dove, Click Step-Growth Polymerization and E/Z Stereochemistry Using Nucleophilic Thiol-yne/-ene Reactions: Applying Old Concepts for Practical Sustainable (Bio)Materials, Acc. Chem. Res. 55 (2022) 2355–2369.
[17] Y. Bicheng, S. Jingzhir, Q. Anjun, T.B. Zhong, Thiol-yne click polymerization, Chin. Sci. Bull. 58 (2013) 2711–2718.

[18] D. Konkolewicz, A. Gray-Weale, S. Perrier, Hyperbranched Polymers by Thiol−Yne Chemistry: From Small Molecules to Functional Polymers, J. Am. Chem. Soc. 131 (2009) 18075–18077.
[19] J.W. Chan, H. Zhou, C.E. Hoyle, A.B. Lowe, Photopolymerization of Thiol-Alkynes: Polysulfide Networks, Chem. Mater. 21 (2009) 1579–1585.
[20] A.B. Cook, R. Barbey, J.A. Burns, S. Perrier, Hyperbranched Polymers with High Degrees of Branching and Low Dispersity Values: Pushing the Limits of Thiol-Yne Chemistry, Macromolecules 49 (2016) 1296–1304.
[21] J. Du, D. Huang, H. Li, A. Qin, B.Z. Tang, Y. Li, Catalyst-Free Click Polymerization of Thiol and Activated Internal Alkynes: A Facile Strategy toward Functional Poly (β-thioacrylate)s, Macromolecules 53 (2020) 4932–4941.
[22] A.B. Lowe, Thiol-yne 'click'/coupling chemistry and recent applications in polymer and materials synthesis and modification, Polymer 55 (2014) 5517–5549.
[23] D. Wang, Q. Guo, H. Gao, Z. Yang, H. Cao, W. He, H. Wang, Facile synthesis of functional poly(vinylene sulfide)s containing donor–acceptor chromophores by a double click reaction, RSC Adv. 6 (2016) 59327–59332.
[24] O. Daglar, S. Luleburgaz, E. Baysak, U.S. Gunay, G. Hizal, U. Tunca, H, Durmaz, Nucleophilic Thiol-yne reaction in Macromolecular Engineering: From synthesis to applications, Eur. Polym. J. 137 (2020), 109926.
[25] C.K.W. Jim, A. Quin, J.W.Y. Lam, F. Mahtab, Y. Yu, B.Z. Tang, Metal-Free Alkyne Polyhydrothiolation: Synthesis of Functional Poly(vinylenesulfide)s with High Stereoregularity by Regioselective Thioclick Polymerization, Adv. Funct. Mater. 20 (2010) 1319–1328.
[26] D. Huang, Y. Liu, S. Guo, B. Li, J. Wang, B. Yao, A. Qin, B.Z. Tang, Transition metal-free thiol–yne click polymerization toward Z-stereoregular poly(vinylene sulfide)s, Polym. Chem. 10 (2019) 3088–3096.
[27] J. Liu, J.W.Y. Lam, C.K.W. Jim, J.C.Y. Ng, J. Shi, H. Su, K.F. Yeung, Y. Hong, M. Faisal, Y. Yu, K.S. Wong, B.Z. Tang, Thiol−Yne Click Polymerization: Regio- and Stereoselective Synthesis of Sulfur-Rich Acetylenic Polymers with Controllable Chain Conformations and Tunable Optical Properties, Macromolecules 44 (2011) 68–79.
[28] B. Yao, J. Mei, J. Li, J. Wang, H. Wu, J. Zhi Sun, A. Qin, B.Z. Tang, Catalyst-Free Thiol-Yne Click Polymerization: A Powerful and Facile Tool for Preparation of Functional Poly(vinylene sulfide)s, Macromolecules 47 (2014) 1325–1333.
[29] B. Yao, T. Hu, H. Zhang, J. Li, J.Z. Sun, A. Qin, B.Z. Tang, Multi-Functional Hyperbranched Poly(vinylene sulfide)s Constructed via Spontaneous Thiol-Yne Click Polymerization, Macromolecules 48 (2015) 7782–7791.
[30] D. Funes-Hernando, P. Hermosilla, E. Vispe, A. Di Giuseppe, R. Castarlenas, L. A. Oro, J.J. Perez-Torrente, Vinylidene-Based Polymers by Rh(I)-NHC Catalyzed Thiol-yne Click Polymerization: Synthesis Characterization and Post-Polymerization Modification, Polym. Chem. 9 (2018) 1298–1302.
[31] H. Uyama, S. Kobayashi, Chemoselective Ring-Opening Polymerization of a Lactone Having exo-Methylene Group with Lipase Catalysis, Macromolecules 34 (2001) 6554–6556.
[32] D. Takeuchi, S. Kim, K. Osakada, Ring-Opening Polymerization of 1-Methylene-2-phenylcyclopropane Catalyzed by a Pd Complex to Afford Regioregulated Polymers, Angew. Chem. Int. Ed. 40 (2001) 2685–2688.
[33] S. Sinnwell, H. Ritter, Ring-Opening Homo- and Copolymerization of α-Methylene-ε-caprolactone, Macromolecules 39 (2006) 2804–2807.
[34] T. Koizumi, K. Sugie, O. Kiyonaga, M. Yamanaka, S. Kawabata, Novel Palladium-Catalyzed Polycondensation of Propargyl Carbonates and Bisphenols Synthesis of Polyethers Having Exomethylene Groups, Macromolecules 37 (2004) 9670–9672.
[35] H. Nishino, N. Nishioka, T. Koizumi, Polycondensation behavior between propargyl carbonates having a bulky ester group and bisphenols in the presence of Pd(0) catalyst: synthesis of exomethylene-containing polyethers, Polym. J. 44 (2012) 321–326.
[36] M. Nishiura, Z. Hou, Organolanthanide catalyzed regio- and stereoselective dimerization of terminal alkynes and polymerization of aromatic diynes, J. Mol. Catal. A: Chem. 213 (2004) 101–106.
[37] H. Katayama, M. Nakayama, T. Nakano, C. Wada, K. Akamatsu, F. Ozawa, Polyaddition of 2,7-Diethynyl-9,9-dioctylfluorene Using Regio- and Stereoselective Alkyne Dimerization Catalysts, Macromolecules 37 (2004) 13–17.
[38] A. Di Giuseppe, R. Castarlenas, J.J. Pérez-Torrente, M. Crucianelli, V. Polo, R. Sancho, F.J. Lahoz, L.A. Oro, Ligand-Controlled Regioselectivity in the Hydrothiolation of Alkynes by Rhodium N-Heterocyclic Carbene Catalysts, J. Am. Chem. Soc. 134 (2012) 8171–8183.
[39] R. Castarlenas, A. Di Giuseppe, J.J. Pérez-Torrente, L.A. Oro, The Emergence of Transition-Metal-Mediated Hydrothiolation of Unsaturated Carbon-Carbon Bonds: A Mechanistic Outlook, Angew. Chem. Int. Ed. 52 (2013) 211–222.
[40] L. Palacios, M.J. Artigas, V. Polo, F.J. Lahoz, R. Castarlenas, J.J. Pérez-Torrente, L. A. Oro, Hydroxo-Rhodium-N-Heterocyclic Carbene Complexes as Efficient Catalyst Precursors for Alkyne Hydrothiolation, ACS Catal. 3 (2013) 2910–2919.
[41] L. Palacios, A. Di Giuseppe, M.J. Artigas, V. Polo, F.J. Lahoz, R. Castarlenas, J. J. Pérez-Torrente, L.A. Oro, Mechanistic Insight into the Pyridine Enhanced α-Selectivity in Alkyne Hydrothiolation Catalysed by Quinolinolate-Rhodium(i)-N-Heterocyclic Carbene Complexes, Catal. Sci. Technol. 6 (2016) 8548–8561.
[42] L. Palacios, Y. Meheut, M. Galiana-Cameo, M.J. Artigas, A. Di Giuseppe, F.J. Lahoz, V. Polo, R. Castarlenas, J.J. Pérez- Torrente, L.A. Oro, Design of Highly Selective Alkyne Hydrothiolation RhINHC Catalysts: Carbonyl-Triggered Nonoxidative Mechanism, Organometallics 36 (2017) 2198–2207.
[43] R.M. Silverstein, F.X. Webster, D.J. Kiemle, Spectrometric Identification of Organic Compounds, 7th ed, John Wiley & Sons, Hoboken, New Jersey, 2005.
[44] X.-Y. Yu, B.O. Patrick, B.R. James, Rhodium(III) peroxo complexes containing carbene and phosphine ligands, Organometallics 25 (2006) 4870–4877.
[45] S. Podzimek, Light scattering, size exclusion chromatography and asymmetric flow field flow fractionation, John Wiley and Sons, Hoboken, New Jersey, 2011, pp. 65–72.
[46] W.F. Reed, A.M. Alb, Monitoring polymerization reactions: from fundamentals to applications, John Wiley & Sons, Hoboken, New Jersey, 2014.
[47] A.M. Alb, M.F. Drenski, W.F. Reed, Simultaneous continuous, nonchromatographic monitoring and discrete chromatographic monitoring of polymerization reactions, J. Appl. Polym. Sci. 113 (2009) 190–198.