

Synergetic Effect of Monomer Functional Group Coordination in Catalytic Insertion Polymerization

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S Supporting Information

ABSTRACT: PhS- and PhNH-functionalized dienes are copolymerized efficiently with butadiene to stereoregular copolymers by [(mesitylene)Ni(allyl)][BAr^F₄] (Ni-1). Overall polymerization rates and comonomer incorporations depend strongly on the linker length between the diene moiety and functional group, in, e.g., PhS—(CH₂)_xC(=CH₂)—CH=CH₂ (**PhS-x-BD**, x = 3-7), in particular for certain linker lengths high comonomer reactivity ratios stand out. This effect is related to a favorable binding of the comonomer to the active site comprising coordination of its functional group, which significantly enhances comonomer incorporation in the growing polymer chain.

 ${f S}$ ince their inception by Ziegler and Natta, catalytic insertion polymerizations have advanced to one of the largest scale synthetic reactions carried out today. This is due to the ability to control materials properties via the polymer microstructures. Within this established scenario, an incorporation of polar vinyl monomers remains challenging. Over the past 2 decades, less oxophilic late transition metal catalysts have been discovered that enable the copolymerization of ethylene with a wide variety of polar vinyl monomers.^{1–7} Concerning stereoselective polymerizations, only recently Nozaki⁸ et al. have reported advances toward functionalized poly(propylenes) and we⁹ and Cui¹⁰ et al. have reported stereoregular functionalized poly-(dienes) and poly(methoxystyrenes)^{11,12} from insertion copolymerization.

Although an incorporation of polar and reactive groups in the polymer is desirable in terms of its materials properties, during polymerization it has adverse effects exclusively. Thus, in the mechanistically well understood copolymerizations of ethylene with polar vinyl monomers, polymerization rates and polymer molecular weights are reduced by the presence of comonomer. This effect has been traced to κ -X coordination of the functional group of free comonomer or already incorporated comonomer-derived repeat units. The functional group reversibly blocks coordination sites for further chain growth. Further, this adverse effect of the free monomers' functional groups is all the more relevant, as copolymerization parameters disfavor comonomer incorporation, such that high comonomer concentrations are required even if comonomer conversion remains low.^{13–17}

We now for the first time provide evidence how precoordination of the comonomers' functional groups can

have a beneficial impact on monomer incorporations and copolymerization rates.

Recently, $[(\text{mesitylene})\text{Ni}(\text{allyl})][\text{BAr}_4^{F}]$ (Ni-1)^{18,19} was found to be capable of copolymerizing a variety of silicon-, boron-, nitrogen-, oxygen-, and phosphorus-based polar dienemonomers with 1,3-butadiene (BD) or isoprene (IP), providing access to functionalized 1,4-*cis*-poly(butadiene) copolymers.² Comonomer conversion is persistently high in these copolymerizations, even at low comonomer concentrations. Additionally, qualitative NMR experiments suggested monomer reactivity ratios of $r = k_{\text{CoMo}}/k_{\text{BD}} > 1$.

Such favorable comonomer incorporation is remarkable, but its origin is ill understood. To gain more insight into the copolymerization behavior of polar functionalized dienes and the contributions of the functional groups, we studied dienes with different functional groups and different linker lengths (Chart 1, for detailed synthetic procedures cf. SI). A possible

Chart 1. Dienes and Model Compounds Used in (Co)polymerizations with Butadiene



(beneficial) interaction of the functional group with the catalyst should be reflected by a dependence on the linker length itself and also on the coordination strength of the heteroatom.

Copolymerization experiments with the entire range of PhSfunctionalized comonomers showed that **Ni-1** is tolerant toward the functional group, resulting in the first stereoselective copolymerization of sulfur-functionalized dienes with BD. From

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monitoring of the copolymerization by ¹H NMR spectroscopy (cf. SI for detailed data), a significant influence of the comonomer on the copolymerizations can be observed. A kinetic plot of the copolymerization of BD with **PhS-3-BD** reveals a change of the first-order rate constant for butadiene consumption from $k_{\rm BD} = 0.16 \times 10^{-3} \text{ s}^{-1}$ to $k'_{\rm BD} = 3.7 \times 10^{-3} \text{ s}^{-1}$ after 60 h reaction time (Figure 1 and Table 1). This



Figure 1. First-order kinetic plots of the copolymerizations of BD with PhS-3-BD or PhNH-3-BD catalyzed by Ni-1 at 40 $^{\circ}$ C.

significant, ca. 20-fold, increase of polymerization activity coincides with the complete consumption, i.e., incorporation of the entire amount of **PhS-3-BD** present in this experiment.^{20,21} When the initial (copolymerization) rate constants $k_{\rm BD}$ and $k_{\rm CoMo}$ are compared, a monomer reactivity ratio of $k_{\rm CoMo}/k_{\rm BD} = r_{\rm CoMo} = 4.6$ in favor of **PhS-3-BD** is found.

Strikingly, BD consumption has a significantly increased rate constant ($k_{\rm BD} = 4.4 \times 10^{-3} \, {\rm s}^{-1}$) in the presence of **PhS-4-BD** that is 1 order of magnitude greater than the initial rate constant for **PhS-3-BD**, while still exhibiting a comparable strong preference for the incorporation of the comonomer ($r_{\rm CoMo} = 4.9$).

For linker lengths longer than four methylene units, the rate constants are slightly higher with a maximum observed for **PhS-6-BD** ($k_{\rm BD} = 9.0 \times 10^{-3} \text{ s}^{-1}$).

However, the monomer reactivity ratios are all similar ($r_{CoMo} = 1.6-1.7$) and clearly lower when compared to those of **PhS-3-BD** or **PhS-4-BD**.

To further illustrate these experiments and also for comparison with other data (vide infra), incorporation of **PhS-3-BD** is complete at only 16% BD consumption (after ca. 60 h at 40 °C) resulting in a copolymer with a comonomer:BD ratio of 60:40. Under these conditions, it takes 5–6 days to reach >95% overall diene consumption (and the copolymer formed is expected to exhibit a gradient copolymer structure).

Table 1. Rate Constants Obtained from Kinetic NMR Experiments for (Co)polymerizations of BD with Different Comonomers and Model Compounds Catalyzed by Ni-1

entry	CoMo/additive	$k_{\rm BD} \; [10^{-3} \; {\rm s}^{-1}]$	$k_{\rm CoMo} \; [10^{-3} \; {\rm s}^{-1}]$	r _{CoMo} ^a
1-1 ^b	PhS-3-BD	0.16	0.74	4.6
1-2 ^c	PhS-4-BD	4.4	21	4.9
1-3 ^c	PhS-5-BD	5.6	9.1	1.6
1-4 ^c	PhS-6-BD	9.0	15	1.7
1-5 ^c	PhS-7-BD	4.7	7.6	1.6
1-6 ^d	PhNH-3-BD	0.086	0.683	7.90
1-7 ^d	PhNH-6-BD	32.6	40.6	1.3
1-8 ^e	5-BD	n.a. ⁱ	n.a. ⁱ	2.2
1-9 ^e	IP	n.a. ⁱ	n.a. ⁱ	1.2
1-10 ^f	PhS-6	49		
1-11 ^g	PhNH-3	40		
1-12 ^h	PhS-4-Ene	28		
1-13 ^h	PhS-6-Ene	83		
1-14 ^h	PhS-8-Ene	78		
1-15 ⁱ	_j	>6000		

^aMonomer reactivity ratio $r_{\rm CoM0} = k_{\rm CoM0}/k_{\rm BD}$. ^bNi:BD:CoMo = 1:120:24, T = 40 °C. ^cNi:BD:CoMo = ca. 1:400:60, T = 40 °C. ^dNi:BD:CoMo = ca. 1:400:75, T = 40 °C. ^eNi:BD:CoMo = ca. 1:200:30, T = -15 °C. ^fNi:BD:additive = ca. 1:400:60, T = 40 °C. ^gNi:BD:additive = 1:120:28, T = 40 °C. ^hNi:BD:additive = ca. 1:400:75, T = 40 °C. ⁱNot applicable, as reactions were conducted at a different temperature. ^j $k_{\rm BD}$ was calculated for a BD homopolymerization from the observation that BD conversion reaches >99.5% after 5 min at 40 °C.

This high preference for the incorporation of a sulfur containing monomer was also observed in a copolymerization with **PhS-4-BD**. The entire comonomer present is already incorporated at a BD consumption of 50% (after only 3 h at 40 °C) resulting in a copolymer with a comonomer:BD ratio of 30:70. However, >95% overall diene consumption is now reached after only 6 h opposed to 6 days for the copolymerization of **PhS-3-BD** although the dienes:Ni ratio is higher. In contrast, the preference for insertion of **PhS-5-BD**, **PhS-6-BD**, or **PhS-7-BD** vs butadiene-insertion is not that pronounced as evidenced by complete comonomer consumptions at 93% (**PhS-5-BD**), 94% (**PhS-6-BD**), and 93% (**PhS-7-BD**) BD consumption.^{20,22}

These observed effects are even more pronounced for copolymerizations with comonomers bearing a supposedly even stronger coordinating PhNH-group. Although the copolymerization of **PhNH-3-BD** takes ca. 10 days to reach >68% diene conversion, the copolymerization of **PhNH-6-BD** only takes ca. 2-3 h for the same conversion under otherwise identical conditions.

Again, an obvious change of the rate constant for the consumption of BD is visible, once **PhNH-3-BD** is completely consumed (Figure 1).²⁰ The rate constant in the absence of free comonomer ($k'_{BD} = 3.95 \times 10^{-3} \text{ s}^{-1}$) is ca. 50 times increased compared to the rate constant at the beginning of the polymerization ($k_{BD} = 0.086 \times 10^{-3} \text{ s}^{-1}$).

Comparison of the initial rate constants of BD and comonomer consumption reveals a monomer reactivity ratio of $r_{\text{CoMo}} = 7.9$. Increasing the linker length to six methylene units in **PhNH-6-BD** results in a ca. 380-fold increased rate constant for the BD incorporation, whereas the monomer reactivity ratio drops from 7.9 to 1.3.

The influence of linker lengths on rate constants and monomer reactivity ratio can also be found in a less

Figure 2. Influence of *κ*-X assisted precoordination and different linker lengths on polymerization activity and comonomer insertion.

pronounced fashion for sterically more hindered, i.e., weaker coordinating, Ph₂N- and TMS₂N- groups. A general increase of rate constants (BD incorporation as well as comonomer incorporation) is observed for copolymerizations in the presence of weaker coordinating groups and reflected in lower overall reaction times. Rate constants range from $k_{\rm BD} = 57.5 \times 10^{-3} \, {\rm s}^{-1}$ to $k_{\rm BD} = 80.5 \times 10^{-3} \, {\rm s}^{-1}$ for copolymerization with Ph₂N-x-BD (x = 3, 4, 6) and from $k_{\rm BD} = 31.2 \times 10^{-3} \, {\rm s}^{-1}$ to $k_{\rm BD} = 123.7 \times 10^{-3} \, {\rm s}^{-1}$ for the entire range of linker lengths from TMS₂N-3-BD to TMS₂N-6-BD (cf. SI, Table S1). At the same time, the preference for comonomer insertion is reduced and monomer reactivity ratios between $r_{\rm CoMo} = 0.8$ and $r_{\rm CoMo} = 1.5$ are observed.²³

Different mechanistic scenarios can rationalize the remarkably favorable comonomer reactivity ratios at certain linker lengths: (a) A favored incorporation is only caused by the comonomer's linker substituent and not by the presence of Lewis basic heteroatoms, i.e., even a nonfunctionalized 2hydrocarbyl substituted 1,3-butadiene shows an enhanced incorporation. (b) A Lewis acid Lewis base interaction, i.e., κ -X coordination, between the catalytically active metal center and the heteroatom on the comonomer (acting as a ligand) is responsible for an enhanced comonomer incorporation. This consideration may be extended to the formation of a chelate by simultaneous κ -X and η^4 -diene coordination of one comonomer unit. (c) A combination of mechanistic scenarios a and b is responsible. Suitable nonpolymerizable model compounds were employed to assess the different contributions of the functional group (PhS-6, PhNH-3), the comonomer's linker substituent (5-BD), or postinsertion inhibition (PhS-x-Ene, x = 4, 6, 8) separately.

The influence of scenario (a) was probed in copolymerizations of BD and IP or 5-BD. A benchmark homopolymerization of BD and copolymerizations of BD with IP or 5-BD could not be followed at 40 °C because they were too fast. Hence, these reactions were conducted at a lower temperature of -15°C. For IP and 5-BD, >95% BD consumption is reached already after ca. 2-3 h at 258 K, with an observed slight preference for the incorporation of the comonomer (monomer reactivity ratios $r_{\rm IP} = 1.2$, $r_{5-\rm BD} = 2.2$) whereas BD homopolymerization had already reached 80% BD conversion when the sample was inserted into the NMR probe, and >95% BD consumption was reached after an additional ca. 20 min at -15 °C. Thus, the substitution of the diene moiety at the 2position results in a decreased polymerization activity compared to a BD homopolymerization as well as a slightly preferred incorporation of the substituted diene. However, a profoundly increased comonomer reactivity ratio as observed for, e.g., PhS-3-BD, is not observed, therefore excluding scenario (a) as the prime reason for enhanced comonomer incorporation.

Concerning scenario (b), to elucidate the effect of κ -X coordination alone, control polymerizations of BD in the

presence of hexyl thiophenol ether or *N*-propylaniline (**PhS-6** and **PhNH-3**) were performed under similar conditions. The reactions reach >95% BD consumption already after 60 min (**PhS-6**, $k_{\rm BD} = 49 \times 10^{-3} \, {\rm s}^{-1}$) and 90 min (**PhNH-3**, $k_{\rm BD} = 40 \times 10^{-3} \, {\rm s}^{-1}$). The rate constant of the polymerization in the presence of **PhNH-3** is ca. 460-fold increased compared to the rate constant of the copolymerization with **PhNH-3-BD**, thus ruling out κ -X coordination as the only cause for such dramatic differences in overall polymerization rates and indicating a simultaneous κ -X and η^4 -diene coordination instead.

The influence of an already incorporated comonomer unit in the polymer chain on the polymerization was probed in polymerizations of BD in the presence of the model compounds **PhS-4-Ene**, **PhS-6-Ene**, and **PhS-8-Ene**. These 1olefins qualitatively resemble the polymer chain in the sense that they can coordinate through their olefin functions as well as polar groups.²⁴ Kinetic evaluations of these polymerizations show that the rate constants are significantly higher compared to the rate constants of the copolymerization (Table 1, entries 1-12, 1-13, and 1-14). For example, a BD conversion >95% was observed after 96 min in the presence of **PhS-8-Ene**, thus excluding an extensive inhibition of the polymerization by an already incorporated comonomer unit.

As a conclusion from these observations, mimics of the functional group (like **PhS-6** or **PhNH-3**) slow down the polymerization. That is, free monomer and functional groups of formed polymer present in the reaction solution can interact with the metal center, without the involvement of further binding sites (like the same comonomer molecules' double bonds). However, this can not account for the different behavior of monomers with different linker lengths.

From copolymerizations of ethylene with polar vinyl monomers, it is well understood that a κ -X coordination of the functional group of the last or penultimate incorporated comonomer-derived repeat unit is the most relevant reason for decreased polymerization rates.

Depending on a possible η^4 -diene coordination, the conformation, and therefore the reactivity of the resulting species, this can have different implications: First, if insertion does not occur through the κ -X coordinated species but other pathways, the copolymerization is slowed down and the comonomer incorporation is not affected (Figure 2, case 1). Second, if insertion is viable, the scenario can account for κ -X assisted, increased comonomer incorporation as observed prominently for PhS-3-BD, PhS-4-BD, and PhNH-3-BD.

Importantly, here the linker length will affect the ground state of the coordinated starting species (cf. Figure 2 cases 2 and 3), the transition state, and intermediate species involved in the polymerization. This affects the comonomer insertion step as illustrated by **PhS-3-BD** and **PhS-4-BD**. Both are incorporated preferentially, but the copolymerization is much faster in the case of the latter (Figure 2, case 2 vs 3). Although geometries of responsible ground- or transition states are

worthwhile issues of interest, the presence and operation of a κ -X assisted, enhanced incorporation is clearly evident.

In conclusion, we have observed severe effects of different functional groups and linker lengths on polymerization rate constants and monomer reactivity ratios in copolymerizations of BD and polar functionalized dienes catalyzed by Ni-1. Although certain linker lengths lead to an unprecedented preference for the incorporation of the polar functionalized diene, all obtained copolymers are stereoregular (cf. SI). Depending on the linker length, the strong enhancement of incorporation is accompanied by a severe or moderate decrease of the polymerization rate vs BD homopolymerization. For other "nonmatched" linker lengths, the incorporation of the comonomer is only slightly favored while at the same time polymerization rates are only moderately influenced. The correct choice of a suitable linker length thus enables a facile copolymerization of dienes functionalized with difficult polar moieties including PhS- or even PhNH- groups. We suggest that this remarkable behavior results from a κ -X assisted precoordination of the functional group to the metal center based on kinetic NMR experiments with various comonomers and model compounds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b03087.

> Kinetic plots, synthetic procedures, and selected NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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(20) The virtually complete comonomer consumption was determined by the absence of olefinic comonomer signals in the ¹H NMR spectra.

(21) Please note that this corresponds at the same time to a gradual transition from a copolymerization of BD and PhS-3-BD to a mere homopolymerization of BD, thus rationalizing the description of this behavior by determination of two different rate constants for the two distinct (co)polymerization regimes.

(22) Note that in these experiments the initial ratio of BD:comonomer is ca. 5:1 and the BD:comonomer ratio increases significantly during the polymerization. That is, the incorporation of comonomer is still favored as also reflected by $k_{\text{CoMo}}/k_{\text{BD}} = r_{\text{CoMo}} > 1$ for all comonomers described in this example.

(23) Note for these copolymerizations that the polymerization behavior deviates in some cases significantly from first-order behavior for so far unknown reasons.

(24) Note that in detail, the 1-olefin function will coordinate stronger than a trisubstituted olefinic moiety of the polymer backbone. Also, these model compounds rather resemble the coordination behavior of an arbitrary, incorporated comonomer unit in the polymer backbone than an ultimately incorporated comonomer unit as they can not simulate a possible involved metal-comonomer bond. Notwithstanding, the essential feature of a potential bidentate κ -S, η^2 -olefin coordination is reflected.