

Controlled Polymerization in Polar Solvents to Ultrahigh Molecular Weight Polyethylene

Philip Kenyon,[®] Melissa Wörner, and Stefan Mecking^{*®}

Chemical Materials Science, Department of Chemistry, University of Konstanz, Universitätsstrasse 10, 78457 Konstanz, Germany

S Supporting Information

ABSTRACT: Novel complexes based on 2,4,8-triarylnaphthylamine [[(2,4-{3,5-(CF₃)₂C₆H₃}₂-8-(3,5-R₂C₆H₃)-C₁₀H₄)—N=C(H)—{3-(9-anthryl)-2-O-C₆H₃}- κ^2 -N,O]Ni(CH₃)(pyridine)] (4-Py, R = Me; 5-Py, R = CF₃) were synthesized from 8-arylnaphthylamines which can be generated via selective lithiation, borylation, and coupling in a one-pot procedure. Due to their living characteristics in ethylene polymerization and the particularly low propensity of 5-Py for β -H elimination as reflected by a high linearity even at elevated polymerization temperatures of 60 °C, ultrahigh molecular weight polyethylene (UHMWPE)



is formed in polar organic solvents (THF, diethyl ether) as a reaction medium in a controlled polymerization ($M_w/M_n = 1.2$ at $M_n = 1.1 \times 10^6$ g mol⁻¹).

INTRODUCTION

The reaction medium or solvent is of paramount importance for any chemical reaction. This is particularly pronounced for polymerization reactions. Here, not only do reactions and interactions of the solvent with reactive species like catalysts or initiators occur, but the reaction medium also affects the product morphology.¹ Organic reaction media and solvents for catalytic polymerization are restricted to hydrocarbons (or halogenated solvents) to date, however. This is related to the incompatibility of traditional polymerization catalysts with compounds containing other heteroatoms.²

Less electrophilic late transition metals are much more tolerant in this regard. This has been well recognized for the copolymerization of ethylene with polar vinyl monomers.^{3–16} From these studies, a conclusive picture has evolved on how different functional groups interact with the polymerization active metal sites.¹⁷

Due to the propensity of late transition metal alkyl complexes for β -H elimination, chain transfer often limits molecular weights and much effort has been devoted to the design of catalysts that nonetheless can provide high molecular weight polymers.^{10–12,15,16,18–25} Although no comprehensive picture exists, it appears that high concentrations of coordinating compounds tend to reduce polymer molecular weights, likely by hindering chain growth or even by actively promoting chain transfer.

A particular case regarding reaction media for insertion polymerization are aqueous polymerizations,²⁶ enabled by the water-tolerance of neutral Ni(II) salicylaldiminato complexes.^{27,28} Starting from water-soluble complexes like ^{CF3}1-L or 2-L (cf. Figure 1, L = water-soluble ligand instead of pyridine), surfactant-stabilized single lamella polyethylene nanoscale crystals are formed. The particular aqueous particle formation process suppresses the formation of entanglements.²⁶

© XXXX American Chemical Society



Figure 1. Terphenyl-based catalysts ^{Me}1-Py and ^{CF3}1-Py and 2-Py, a terphenyl derivative for high molecular weights.

This is of interest among others to improve the processing properties of ultrahigh molecular weight polyethylene (UHMWPE).²⁹ Nascent nonentangled morphologies have been much sought to this end, traditionally limited to hydrocarbon reaction media.^{30,31}

A further significant improvement of the N-terphenyl motif of 1 or 2 was achieved with Brookhart's and Daugulis' diarylnaphthylamine-based catalysts like 3-Py. These polymerize ethylene to moderately branched UHMWPE with molecular weights up to 1.4×10^6 g mol⁻¹ and narrow molecular weight distributions, even at elevated temperatures of 60 °C. For the terphenyl system, distal substituents have an extreme effect on the outcome of polymerization. While ^{CF3}1-Py forms linear polyethylene, ^{Me}1-Py yields hyperbranched oligomers. This has recently been recognized to result from a weak Ni… arene interaction that promotes chain transfer and branching in the latter case.³²

Received: March 23, 2018

We now report on living/controlled polymerizations using THF and diethyl ether as a reaction medium where, with enhanced catalysts, UHMWPE can be obtained. The insights on the role of distal substituents³² prompted us to explore the effect of electron-withdrawing substituted bis(trifluoromethyl)-phenyl groups in the 4- and particularly the 8-position of the naphthylamine moiety (**4-Py** and **5-Py**, Figure 2).



Figure 2. Catalyst based on diarylnaphthylamine introduced by Brookhart and Daugulis (3-Py) and novel catalysts based on triarylnaphthylamine (4-Py and 5-Py).

RESULTS AND DISCUSSION

Rather than the previously performed multistep reaction³³ based on C–H activation,³⁴ naphthylamine derivative NA-CF₃ was synthesized in a one-pot reaction beginning with a selective, quantitative lithiation reaction, followed by introducing a boronic acid group. Suzuki coupling with 3,5-bis-(trifluoromethyl)bromobenzene gave NA-CF₃ in an 80% yield (Scheme 1).



2,4,8-Triarylnaphthylamine derivatives were then synthesized in a manner analogous to the previously reported 2,8diarylnaphthylamine derivatives. Selective 2,4-dibromination was followed by Suzuki coupling, and the desired salicylaldimines (4 and 5) were obtained by condensation with the appropriate aldehyde (Scheme 2). Precatalysts (4-Py and 5-Py) were then obtained by reaction with [NiMe₂(TMEDA)] in the presence of excess pyridine (Scheme 3). The polymerization properties of the novel catalyst precursors and 2-Py and 3-Py for comparison were studied over a range of temperatures (40–60 °C; Table 1). It is immediately clear that the naphthylamine-based 3-Py, 4-Py, and 5-Py produce fewer branches than 2-Py under identical reaction conditions (Figure 3). In addition to an apparently reduced propensity for β -H elimination and chain transfer, the lower branching can also be related to a higher steric congestion making insertion of ethylene into secondary alkyls formed via chain walking less favorable. A similar increase in sterics leading to a reduction in branching was observed for diimine palladium catalysts.³⁵

The introduction of an additional electron-withdrawing substituted aryl that points away from the metal center (in the 4-position) does not have a notable impact on branching. At a given temperature, **3-Py** and **4-Py** yield essentially identical degrees of branching. Significant differences are observed for **5-Py**, however. At all temperatures, **5-Py** produces a more linear polymer than **4-Py**. Even at 60 °C, only one methyl branch per 1000 C atoms is observed. While this reduction in branches via changing the remote substituent is less dramatic than the change observed for ^{Me}1-Py and ^{CF3}1-Py (vide supra), it suggests that an analogous effect influences the rate of β -H elimination in naphthylamine based catalysts.

Remarkably, polymerizations with 3-Py, 4-Py, and 5-Py exhibit a living character (Table 1, entries 1-3, 5, 6, 8, and 9) as concluded from narrow molecular weight distributions and a consideration of the number of chains formed per metal center present. The molecular weight is therefore limited by the rate of polymerization, with the more active catalysts (3-Py and 4-Py) producing higher molecular weight polymers. At 60 °C, it can be seen that chain transfer does occur (from the number of chains produced, Table 1, entries 4, 7, and 10), but it remains a rare event and the increase in activity compensates for chain transfer. Notably, 5-Py retains a very narrow molecular weight distribution of $M_w/M_n = 1.2$. Attempts were made to carry out polymerizations at 70 °C; however, a constant temperature could not be maintained over the course of the reaction with the setup employed due to the high activity of these catalysts. By comparison, in polymerizations with 2-Py, molecular weights are determined by β -H elimination and the reaction is in the regime of chain transfer, and as expected for this case, molecular weights decrease with increasing polymerization temperature (Table 1, entries 11-13).

Encouraged by the highly controlled nature of these polymerizations and the ability to form highly linear polyethylene at elevated temperature at the same time, polymerizations in THF and diethyl ether as reaction media were studied. These polar, aprotic solvents can coordinate to the metal center, hindering the coordination of ethylene and suppressing polymerization. Indeed, a lower productivity of the catalyst²⁷ and limited molecular weight was observed at the lower end of the temperature range studied (Table 2, entries 2 and 3).

While higher polymerization temperatures can help to overcome the effects of solvent coordination, the reduced chain propagation and relative increase of β -H elimination lead to high rates of chain transfer and low molecular weight polymers as observed for **2-Py** (Table 2, entry 6). Naphthylamine derived catalysts with low rates of chain transfer are therefore unique in allowing polymerization to high molecular weights in THF (or other coordinating solvents). Using these

Scheme 2. Synthesis of 2,4,8-Triarylnaphthylamines and Subsequent Condensation to Salicylaldimines 4 and 5



1, 4, and 5). Compared to polymerizations in toluene, there is a slight but noted decrease in the number-average molecular weight (M_n) for polymerizations in THF. As this decrease is associated with

for polymerizations in THF. As this decrease is associated with a broadening in the molecular weight distribution for **3-Py** and **4-Py**, it could be argued that this is due to increasing precipitation disturbing the controlled polymerization.²¹



Polymerisation Temperature (°C)

Table 1. Ethylene Polymerization Results with Naphthylamine Derivative Complexes 3-Py, 4-Py, and 5-Py and Representative Terphenyl Derivative Complex 2-Py as Precatalysts in Toluene^a

entry	precatalyst	$T(^{\circ}C)$	yield (g)	TOF ^b	$M_{\rm n}^{\ c} (10^3 \ {\rm g/mol})$	$M_{\rm w}/M_{\rm n}^{\ c}$	$T_{\rm m}^{\ d}$ (°C)	crystallinity ^d (%)	branches/1000 C ^e	chains per nickel
1	3-Py	40	3.6	5.09	818	1.2	135	39	1.0	0.9
2 ^f	3-Py	40	6.4	3.06	1232	1.3	132	47	1.2	1.0
3	3-Py	50	5.8	7.75	1021	1.3	130	45	1.9	1.1
4	3-Py	60	16.5	23.6	1437	1.3	125	43	4.5	2.3
5	4-Py	40	3.8	5.39	796	1.3	134	46	1.1	1.0
6	4-Py	50	7.7	11.0	1186	1.3	131	47	1.8	1.3
7	4-Py	60	12.6	21.1	1451	1.3	126	44	4.3	1.8
8	5-Py	40	2.1	2.99	527	1.1	135	53	0.7	0.8
9	5-Py	50	5.4	7.74	885	1.2	132	48	1.0	1.2
10	5-Py	60	11.5	16.4	1206	1.2	131	51	1.2	1.9
11 ^g	2-Py	40	10.0	10.7	287	2.3	128	58	4.2	6.9
12 ^g	2-Py	50	11.8	12.6	32	2.5	118	55	10.6	43
13 ^g	2-Py	60	16.8	18.0	17	2.1	115	57	13.0 ^h	106

^{*a*}Polymerization conditions: 5 μ mol of precatalyst, 100 mL of toluene, 40 bar of C₂H₄, 30 min. ^{*b*}10⁴ × mol [C₂H₄] × mol⁻¹ [Ni] × h⁻¹. ^{*c*}Determined by GPC at 160 °C. ^{*d*}Determined by DSC. ^{*c*}Determined by ¹³C NMR spectroscopy. ^{*f*}Polymerization carried out for 90 min. ^{*g*}Polymerization carried out for 40 min. ^{*h*}Includes 0.6 ethyl and 0.4 *n*-propyl branches.

Table 2	. Ethylene	Polymeriz	ation R	lesults with	Naphthylamine	Derivative	Complexes	3-Py, 4-I	Py, and 5-Py	and R	epresentative
Terpher	nyl Deriva	tive Comp	lex 2-P	y as Precata	lysts in THF ^a						

entry	precatalyst	$T(^{\circ}C)$	yield (g)	TOF	$M_{\rm n}^{\ c}$ (10 ³ g/mol)	$M_{\rm w}/M_{\rm n}^{\ c}$	$T_{\rm m}^{\ d}$ (°C)	crystallinity ^d (%)	branches/1000 C ^e	chains per nickel
1	3-Py	60	13.4	19.1	1097	1.4	120	44	5.7	2.4
2^{f}	4-Py	35	5.9	2.81	1279	1.2	135	49	0.9	0.7
3 ^g	4-Py	35	1.8	0.88	519	1.4	135	50	1.2	0.9
4	4-Py	60	9.6	13.7	993	1.7	120	46	7.0	1.9
5	5-Py	60	10.1	14.4	1111	1.2	128	52	3.5	1.8
6	2-Py	60	11.2	12.0	5.6	2.1	99	52	26.1 ^h	400

^{*a*}Polymerization conditions: 5 μ mol of precatalyst, 100 mL of THF, 40 bar of C₂H₄, 30 min. ^{*b*}10⁴ × mol [C₂H₄] × mol⁻¹ [Ni] × h⁻¹. ^{*c*}Determined by GPC at 160 °C. ^{*d*}Determined by DSC. ^{*e*}Determined by ¹³C NMR spectroscopy. ^{*f*}Polymerization carried out for 90 min in toluene. ^{*s*}Polymerization carried out for 90 min in diethyl ether. ^{*h*}Includes 1.7 ethyl and 1.0 *n*-propyl branches.

However, the UHMWPE produced by 5-Py retains a narrow molecular weight distribution, suggesting precipitation is not the source of this broadening.

The probable source of molecular weight broadening is an increase in the number of dormant states produced by polymerization in THF (Figure 4). Besides the pyridine



Figure 4. Proposed dormant states in THF for naphthylamine derived catalysts. Ar = 2,8-diarylnaphthylamine (3-Py) or 2,4,8-triarylnaphthylamine (4-Py, 5-Py).

coordinated resting state (formed by the recombination of the equivalent of pyridine introduced with the catalyst) observed by NMR previously,²¹ a species with coordinated THF is present and due to the increase in β -H elimination chain walking species become more common.

As **5-Py** shows similar productivity in THF and toluene, the formation of THF coordinated species seems to be less significant than that for **3-Py** and **4-Py**. The lowest rates of β -H elimination are also observed for **5-Py**, suggesting that chain walking is also minimized. These remote substituents are therefore the main factor in allowing for controlled polymerization to UHMWPE in THF.

CONCLUSION

Salicylaldiminato catalysts based on arylnaphthylamine derivatives show low rates of β -H elimination and chain transfer which allow for polymerization to lightly branched UHMWPE at high temperatures. The rate of β -H elimination can be reduced by introducing electron-withdrawing (CF₃) substituents on the aryl ring in the 8-position of the naphthylamine backbone. While rare chain transfer events do occur at higher temperatures (i.e., one per active site even at 60 °C), polymerization remains controlled, leading to UHMWPE with narrow molecular weight distributions ($M_w/M_n < 1.3$). At the same time, linear polyethylene with only one branch per 1000 carbon atoms is obtained.

Remarkably, these controlled characteristics are retained in polar solvents as a reaction medium. Compared to toluene, reaction in THF leads to lower molecular weights and broader molecular weight distributions. With the introduction of CF_3 substituents, this can be minimized to allow for polymerization to UHMWPE with a narrow molecular weight distribution in THF. The polarity of the reaction medium and its miscibility with the formed polymer will decisively influence parameters like crystallization rates, and we are currently exploring its impact on morphology. The overcoming of the restriction to hydrocarbon solvents opens up broad opportunities for control of supramolecular structure formation during polymerization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b03223.

Synthetic procedures for the preparation of new ligands and complexes; ¹H, ¹³C, and ¹⁹F NMR spectra for new compounds; procedures for the polymerization of ethylene; examples of ¹H and ¹³C NMR spectra for polymers; DSC traces of polymers produced in THF; GPC traces of UHMWPE produced in THF (PDF)

AUTHOR INFORMATION

Corresponding Author

*Stefan.Mecking@uni-konstanz.de

ORCID 💿

Philip Kenyon: 0000-0003-0244-1347 Stefan Mecking: 0000-0002-6618-6659

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Nic Friederichs and Dieter Bilda for fruitful discussions. We thank Lars Bolk for DSC and GPC analyses and Anke Friemel and Ulrich Haunz for support with NMR measurements. Financial support by SABIC is gratefully acknowledged.

REFERENCES

(1) Stürzel, M.; Mihan, S.; Mülhaupt, R. Chem. Rev. 2016, 116, 1398–1433.

(2) Nakamura, A.; Ito, S.; Nozaki, K. Chem. Rev. 2009, 109, 5215–5244.

(3) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. J. Am. Chem. Soc. 1998, 120, 888-899.

(4) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. J. Am. Chem. Soc. 2007, 129, 8946-8947.

(5) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. J. Am. Chem. Soc. 2007, 129, 8948–8949.

(6) Skupov, K. M.; Piche, L.; Claverie, J. P. *Macromolecules* **2008**, *41*, 2309–2310.

(7) Ito, S.; Munakata, K.; Nakamura, A.; Nozaki, K. J. Am. Chem. Soc. **2009**, 131, 14606–14607.

- (9) Guironnet, D.; Roesle, P.; Rünzi, T.; Göttker-Schnetmann, I.; Mecking, S. J. Am. Chem. Soc. 2009, 131, 422–423.
- (10) Radlauer, M. R.; Buckley, A. K.; Henling, L. M.; Agapie, T. J. Am. Chem. Soc. 2013, 135, 3784–3787.
- (11) Takeuchi, D.; Chiba, Y.; Takano, S.; Osakada, K. Angew. Chem., Int. Ed. 2013, 52, 12536–12540.
- (12) Nakano, R.; Nozaki, K. J. Am. Chem. Soc. 2015, 137, 10934–10937.
- (13) Jian, Z.; Mecking, S. Angew. Chem., Int. Ed. 2015, 54, 15845–15849.
- (14) Jian, Z.; Falivene, L.; Boffa, G.; Sánchez, S. O.; Caporaso, L.;
- Grassi, A.; Mecking, S. Angew. Chem., Int. Ed. 2016, 55, 14378-14383.
- (15) Xin, B. S.; Sato, N.; Tanna, A.; Oishi, Y.; Konishi, Y.; Shimizu, F. J. Am. Chem. Soc. **2017**, 139, 3611–3614.
- (16) Chen, Z.; Leatherman, M. D.; Daugulis, O.; Brookhart, M. J. Am. Chem. Soc. 2017, 139, 16013–16022.
- (17) Nakamura, A.; Anselment, T. M.; Claverie, J.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; van Leeuwen, P. W. N.
- M.; Nozaki, K. Acc. Chem. Res. **2013**, 46, 1438–1449.
- (18) Camacho, D. H.; Guan, Z. Macromolecules 2005, 38, 2544-2546.
- (19) Rhinehart, J. L.; Brown, L. A.; Long, B. K. J. Am. Chem. Soc. **2013**, 135, 16316–16319.
- (20) Zhang, D.; Nadres, E. T.; Brookhart, M.; Daugulis, O. Organometallics 2013, 32, 5136-5143.
- (21) Chen, Z.; Mesgar, M.; White, P. S.; Daugulis, O.; Brookhart, M. ACS Catal. 2015, 5, 631–636.
- (22) Xi, Z.; Bazzi, H. S.; Gladysz, J. A. J. Am. Chem. Soc. 2015, 137, 10930–10933.
- (23) Cai, Z.; Xiao, D.; Do, L. H. J. Am. Chem. Soc. **2015**, 137, 15501–15510.
- (24) Dai, S.; Chen, C. Angew. Chem., Int. Ed. 2016, 55, 13281–13285.
 (25) Li, M.; Wang, X.; Luo, Y.; Chen, C. Angew. Chem., Int. Ed. 2017,
- 56, 11604–11609.
- (26) Osichow, A.; Rabe, C.; Vogtt, K.; Narayanan, T.; Harnau, L.; Drechsler, M.; Ballauff, M.; Mecking, S. J. Am. Chem. Soc. **2013**, 135, 11645–11650.
- (27) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460–462.
- (28) Mu, H.; Pan, L.; Song, D.; Li, Y. Chem. Rev. 2015, 115, 12091-12137.
- (29) Kenyon, P.; Mecking, S. J. Am. Chem. Soc. 2017, 139, 13786–13790.
- (30) Rastogi, S.; Yao, Y.; Ronca, S.; Bos, J.; van der Eem, J. *Macromolecules* **2011**, *44*, 5558–5568.
- (31) Ronca, S.; Forte, G.; Ailianou, A.; Kornfield, J. A.; Rastogi, S. ACS Macro Lett. **2012**, *1*, 1116–1120.
- (32) Falivene, L.; Wiedemann, T.; Göttker-Schnetmann, I.; Caporaso, L.; Cavallo, L.; Mecking, S. J. Am. Chem. Soc. 2018, 140, 1305–1312.
- (33) Vaidya, T.; Klimovica, K.; LaPointe, A. M.; Keresztes, I.; Lobkovsky, E. B.; Daugulis, O.; Coates, G. W. J. Am. Chem. Soc. 2014, 136, 7213–7216.
- (34) Nadres, E. T.; Santos, G. F. I.; Shabashov, D.; Daugulis, O. J. Org. Chem. 2013, 78, 9689–9714.
- (35) Dai, S.; Zhou, S.; Zhang, W.; Chen, C. Macromolecules 2016, 49, 8855–8862.