Macromolecules **2006,** *39,* 5995−6002

Copolymerization of Ethylene with 1-Butene and Norbornene to Higher Molecular Weight Copolymers in Aqueous Emulsion

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Received April 11, 2006; Revised Manuscript Received June 5, 2006

ABSTRACT: Ethylene/norbornene and ethylene/1-butene copolymerization with nickel(II) salicylaldiminato complexes [{κ^2-*N*,*O*-6-C(H)═N(2,6-$R_2C_6H_3$)-2,4-$R'_2C_6H_2O$}NiMe(pyridine)] (**1a**, R = 3,5-$Me_2C_6H_3$, R′ = I; **1b**, R,R′ = 3,5-$(F_3C)_2C_6H_3$; **1c**, R = 3,5-$(F_3C)_2C_6H_3$, R′ = I; **2**, R = ^{i}Pr, R′ = I) were studied in toluene as a reaction medium and in emulsion, the latter affording polymer dispersions. High molecular weight copolymers ($M_n > 10^4$ g mol^{-1}) are formed. Incorporation of ethylene is much preferred over butene incorporation, X_{Bu}/x_{Bu} ∼0.05 under typical reaction conditions, by comparison incorporation of the strained olefin norbornene is higher, X_{NB}/x_{NB} ∼0.25 (X = comonomer mole fraction in polymer; x = comonomer mole fraction in reaction mixture). Dispersions contained copolymers with up to 6 mol % comonomer (12 wt % for 1-butene; 20 wt % for norbornene). Incorporation of a few mol % of norbornene strongly decreases polymer crystallinity, which enhances the film forming properties of dispersions. Microstructure analysis by ^{13}C NMR shows that butene is incorporated in a 1,2-, 1,3- and 1,4-fashion. Whether 1,2- or 1,3-incorporation is predominant depends on the catalyst (nature of R).

Introduction

Emulsion polymerization is among the most important and versatile polymerization processes.[1] About 10 million tons of polymer latices are produced annually for a variety of applications, such as coatings and paints. A key step in most applications is film formation upon evaporation of the dispersing medium, rendering aqueous dispersions particularly environmentally benign.

To date, polymer latices are produced industrially by free-radical polymerization exclusively. The range of polymer microstructures accessible and corresponding materials properties is limited.[2] For example, the synthesis of dispersions of saturated inert polymers, which do not bear functional groups sensitive to slow hydrolysis, is a challenge.[1] The synthesis of dispersions from simple olefins directly obtained from cracking of hydrocarbon feedstocks, without the need for further energy and raw material consuming conversion to other monomers (such as acrylates or vinyl acetate), is desirable.[3] In contrast to free radical routes, catalytic polymerization enables control of microstructures over a wide range. We and Spitz and Claverie et al. have recently reported on the synthesis of polyethylene dispersions by nickel(II)-catalyzed polymerization in emulsion, and on their properties.[4−6] With nickel(II) phosphinoenolate complexes, latices of linear polyethylenes of low molecular weight are obtained with average catalyst activities as high as 10^5 TO h^{-1} (TO = turnover, mol(ethylene converted) mol(Ni)$^{-1}$).[5b] Copolymerization with 1-olefins such as 1-hexene or 1-hexadecene, with styrene or even with functionalized olefins such as undec-10-en-1-ol is also possible, affording stable latices of linear ethylene copolymers.[5c] However, molecular weights of the copolymers are very low ($M_n \leq 2 \times 10^3$ g mol^{-1}), and in some cases, it is debatable whether they are true polymers or should be considered as higher oligomers.[5c]

By comparison, nickel(II) salicylaldiminato complexes provide access to latices of higher molecular weight ethylene homopolymers (M_n up to 10^5 g mol^{-1}). We now give a first full account on the control of branching and thus polymer crystallinity in the latices obtained by copolymerization, employing a recently reported novel class of very active salicylaldiminato catalysts.[4f,11]

Results and Discussion

In ethylene homopolymerization with complexes of type **1**, the remote substituents R were found to have a strong influence on the degree of branching and the molecular weight of the polymer.[4f] As the nature of R is varied, polymers ranging from semicrystalline nearly linear polyethylene (**1c**: 8 branches/1000 C; $M_n = 3.4 \times 10^4$ g mol^{-1}) to highly branched, entirely amorphous material (**1a**: > 70 branches/1000 C; $M_n = 1.6 \times 10^3$ g mol^{-1}) are obtained. Molecular weights correlate with branching, as β-hydride transfer is a key step both for the formation of branches as well as chain transfer; with increased branching, molecular weights of the polyethylenes decrease. Polymerizations in aqueous emulsion afford polyethylene dispersions with high polymerization rates, the crystallinity of the particles being determined by the catalyst. However, also from the practical aspect of controlling crystallinity, introduction of branches by copolymerization with a 1-olefin is attractive. One reason is the possibility to introduce branches without the aforementioned correlation between branching and molecular weight.

Complexes **1a**−**c**, substituted with bulky aryl groups $C_6H_3R_2$ in the 2,6-position of the *N*-aryl group, were employed. In addition to the previously reported compounds **1a** and **1c**, the novel complex **1b** with electron-withdrawing 3,5-$(F_3C)_2C_6H_3$ substituents also on the phenolate moiety was prepared (cf. Experimental Section).[7] Comparative studies with the isopropyl-substituted complex **2** were carried out in some cases.

Ethylene━1-Butene Copolymerization. 1-Butene is attractive to study as a comonomer as any unreacted comonomer can be removed easily and reliable from the dispersions obtained due to its volatility, facilitating their characterization. Also, from

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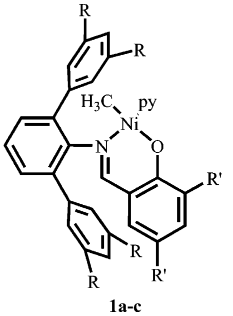
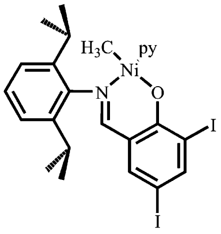
10.1021/ma060813t CCC: $33.50



1a-c

	R	R'
a:	CH_3	I
b:	CF_3	CF_3
c:	CF_3	I

py = pyridine



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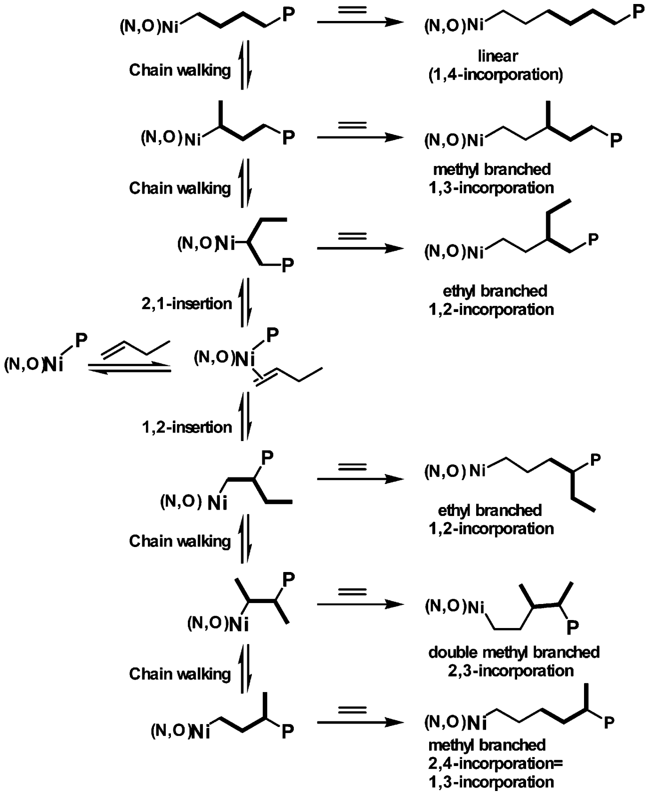
Scheme 1. Possible Modes of Incorporation of 1-Butene into the Polymer Chain



an application point of view 1-butene is attractive due to its low cost.

Copolymerization in Nonaqueous Single Phase. The copolymerization behavior of complexes **1a**−**c** was studied in detail in nonaqueous polymerizations in toluene as a reaction medium (Table 1). In contrast to polymerizations in multiphase aqueous systems, only a single homogeneous liquid phase is present in which the concentrations of the monomers are known. Ethylene concentrations at the polymerization temperature of 50 °C and the pressures of a given experiment were calculated employing the data of Prausnitz et al. for toluene.[8] This involves the reasonable assumption, that in the range of reaction mixture compositions investigated ethylene solubility in the toluene/1-butene mixture does not deviate strongly from the solubility in neat toluene.

For the four different catalyst precursors investigated the incorporation of butene for a given set of reaction conditions does not differ strongly. Ethylene incorporation prevails strongly, the comonomer incorporation in the copolymer X_{Bu} is much lower than the molar ratio x_{Bu} in the reaction mixture, with $X_{Bu} < 0.05\ x_{Bu}$ under the conditions investigated. This trend has also been found by Grubbs et al. for copolymerization of ethylene with 1-olefins by salicylaldiminato Ni complexes.[11b] Catalyst activities are lowered by comparison to ethylene polymerization, the extent depending systematically on the catalyst. For **1a**, which is known to have a strong propensity for 'chain walking′ in ethylene homopolymerization,[4f] activity in 1-butene copolymerization is significantly higher than for **1b**, **1c**, and **2**. Investigations of catalyst activity by monitoring the ethylene flow indicates no significant loss of activity over more than 1 h. Note that for this reason it also appears appropriate to discuss activities in terms of average turn over frequencies (TOF = mol(monomer) mol(Ni)$^{-1}$ h^{-1}; Table 1). The decreased activities in copolymerization appear not to result from an irreversible deactivation of the catalyst by the comonomer or conceivable impurities introduced with the latter, but rather from a slowing of chain growth by a slow insertion of the coordinated relatively bulky butene comonomer, and also to some extent due to a subsequent slow insertion of the next monomer unit into the sterically demanding alkyl species formed (vide infra). The observation that for **1a**, which can more rapidly "chain run" from the bulky alkyl species formed initially by a 1-butene insertion to a less bulky alkyl species prior to the next insertion (cf. Scheme 1), the highest activities in copolymerization are observed seems to indicate that the next monomer insertion after a butene insertion at least partially accounts for the slowing of chain growth by comparison to ethylene polymerization in general.

Copolymerizations in emulsion were carried out by adding a miniemulsion of a solution of the catalyst precursor in a small amount of toluene to a previously prepared (macro) emulsion of 1-butene in water at 50 °C (Table 2). Colloidally stable dispersions were obtained. Polymer molecular weights are up to $M_n = 10^4$ g mol^{-1} as also determined by ^{1}H NMR as an absolute method. Butene incorporations up to 6 mol % (12 wt

Table 1. Nonaqueous Ethylene−Butene Copolymerization[f]

entry	catalyst	p [bar]	x_{butene} in reaction mixture	yield [g]	TOF[e] [TO h^{-1}]	M_n[a] [10^3 g mol^{-1}]	M_w/M_n	Me branches per 1000 C[b]	Et branches per 1000 C[b]	est 1,2-incorp 1-butene[b] [mol %]	est 1,3-incorp 1-butene[b] [mol %]	T_m[c] [°C]	cryst[c] [%]
1−1	**1a**	20	0.76	10.0	9000	0.5	3.3	83	10	0.6	3.5		
1−2	**1a**	40	0.60	22.7	20 000	0.8	2.4	79	8	0.2	2.7		
1−3[d]	**1a**	40		24.0	43 000	1.1	2.1	66	7				
1−4	**1b**	20	0.76	2.7	2400	6.6	2.3	20	17	3.5	0.8	86	25
1−5	**1b**	40	0.60	10.7	9600	11	2.2	17	6	1.2	0.2	101	37
1−6[d]	**1b**	40		17.5	31 000	20	2.3	16				111	45
1−7	**1c**	20	0.76	4.3	3800	19	1.6	14	14	2.9	1.3	98	34
1−8	**1c**	40	0.60	8.4	7500	13	3.7	10	5	1.0	0.4	112	47
1−9[d]	**1c**	40		21.6	39 000	61	3.4	8				125	65
1−10	**2**	20	0.76	3.9	3500	10	2.5	12	10	2.1	1.5	101	34
1−11	**2**	40	0.60	10.0	9000	22	7.2	9	3	0.6	0.8	118	43

[a] Determined by GPC vs linear polyethylene standards. [b] From ^{13}C NMR. [c] From DSC. [d] Polymerization time: 30 min. [e] TOF = average turnover frequency, in mol(olefin converted) mol(Ni)$^{-1}$ h^{-1}. [f] Reaction conditions: 50 mL of toluene, 50 mL of 1-butene; 40 μmol of catalyst precursor; polymerization time, 60 min; temperature, 50 °C.

Table 2. Copolymerization of Ethylene and 1-Butene in Aqueous Emulsion[e]

entry	ethylene pressure [bar]	polymer solids content of dispersion	TOF[d] [TO h^{-1}]	M_n[a] [10^3 g mol^{-1}]	M_w/M_n	particle size [nm]	Me branches per 1000 C[b]	Et branches per 1000 C[b]	est 1,2-incorp 1-butene[b] [mol %]	est 1,3-incorp 1-butene[b] [mol %]	T_m[c] [°C]	cryst[c] [%]
2−1	10	0.2	64	n.d.	n.d.	100	21	45	1.2	4.5	n.d.	n.d.
2−2	20	2.2	723	2.8	3.3	130	20	34	1.1	3.4	76	23
2−3	30	3.3	1076	6.6	5.2	150	16	20	0.6	2.0	94	30
2−4	40	6	2109	11.3	3.1	160	13	12	0.4	1.2	102	35

[a] Determined by GPC vs linear polyethylene standards. [b] From ^{13}C NMR. [c] From DSC. [d] TOF = average turnover frequency, in mol(olefin converted) mol(Ni)$^{-1}$ h^{-1}. [e] Reaction conditions: 98 mL of water, 0.75 g of SDS, 20 mL of 1-butene, 2 mL of toluene, 40 μmol of catalyst precursor **1c**, and polymerization time = 2.5 h.

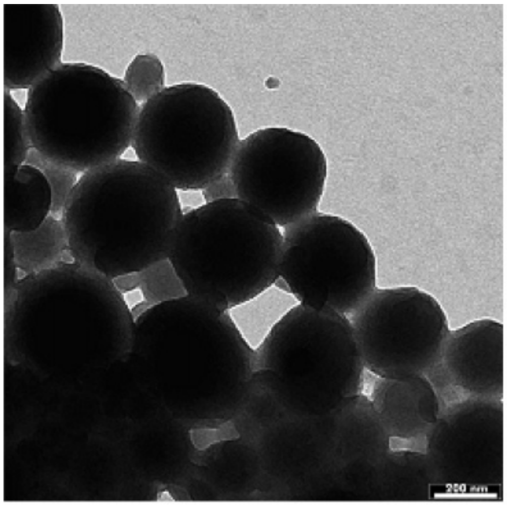


Figure 1. TEM micrograph of an ethylene-1-butene copolymer (X_{Bu} 1 mol %; 11 methyl branches/1000 C; 7 ethyl branches/1000 C. Scale bar is 200 nm.)

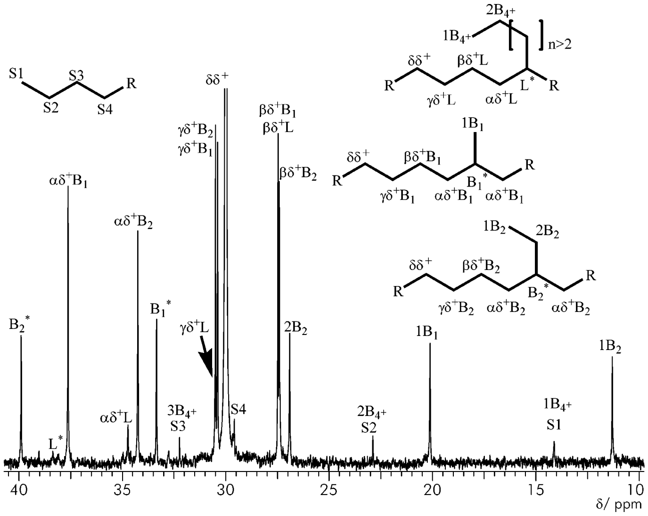


Figure 2. ^{13}C NMR spectrum of an ethylene/1-butene copolymer: 75 MHz; 127 °C; $C_2D_2Cl_4$. Polymer prepared with catalyst precursor **1c**. M_n: 1.9 × 10^4 g mol^{-1}. M_w/M_n = 1.6.

%) were observed under the reaction conditions investigated. Average catalyst activities are considerably lower by comparison to nonaqueous polymerization. However, catalyst activity continues for hours, as evidenced by monitoring of the reaction by means of the ethylene uptake by mass flow metering (Supporting Information). A possible explanation for the lower average activities is an irreversible deactivation of a part of the nickel(II) catalyst during miniemulsification or during the early stages of polymerization.

In TEM micrographs of the latices (Figure 1) discrete particles are observed; i.e., no continuous films are formed during sample preparation for TEM, in accordance with the significant remaining (albeit reduced by comparison to corresponding ethylene homopolymers) crystallinity of the polymer as determined by DSC. In comparison to polyethylene homopolymer particles prepared with the same catalyst under identical conditions, the particle possesses a more spherical structure, which can be related to the reduced crystallinity. The lowered crystallinity results in some film formation at the periphery of the particles (Figure 1). An artifact resulting from surfactant or the like can be excluded, as can be concluded from comparative studies on latices with different sodium dodecyl sulfate (SDS) contents and latices of polymers varying in crystallinity. Evaporating such a dispersion at room temperature affords a transparent film.

Copolymer Microstructure and Properties. Possible modes of incorporation of 1-butene into the polymer chain are depicted in Scheme 1. From microstructure analyses of 1-olefin homopolymers with the same catalysts,[9] it is evident that both 1,2- and 2,1-insertion occur, and from the branched structure of ethylene homopolymers, it is obvious that insertion of ethylene can occur into secondary carbons also. Thus, all modes of insertion depicted are likely to occur to some extent. After a butene insertion, an ethylene insertion is much more likely than another butene insertion, based on statistical considerations from the composition of the copolymer ($X_{\mathrm{ethylene}} \gg X_{\mathrm{Bu}}$); accordingly Scheme 1 depicts this step. Polymer microstructures were analyzed by ^{13}C NMR spectroscopy (Figure 2). 1,3-incorporation (and 2,4-incorporation) of butene result in methyl branches, which are also formed from ethylene monomer alone with all catalysts. 1,2-Incorporation affords ethyl branches. 1,4-Incorporation of butene forms a linear segment, which cannot be differentiated from the polyethylene backbone. An analysis of the copolymer composition and of the modes of incorporation of the 1-butene comonomer (1,2- vs 1,3-incorporation) was carried out on the basis of the reasonable assumption, that the pattern and degree of the ethylene-based branches is the same as in ethylene homopolymerization for a given catalyst and a given temperature and ethylene concentration. For **1a**, which is known to have a strong propensity for chain running in ethylene homopolymerization, indeed 1,3-incorporation of 1-butene clearly prevails over 1,2-incorporation. For the other catalysts investigated, which also yield rather moderately branched polymers in ethylene homopolymerization, 1,2-incorpororation of 1-butene prevails, and a very small amount of higher branches is formed.

Introduction of ethyl branches via the 1-butene comonomer substantially decreases the crystallinity of the semicrystalline polymers formed with catalysts **1b** and **1c**. E.g. by comparison to the corresponding homopolymer (entry 1−6, $M_n = 2 \times 10^4$ g mol^{-1},16 methyl branches/1000 carbon atoms) with a T_m of 111 °C and a crystallinity of ca. 45%, the melting point and crystallinity of the copolymer (entry 1−4, $M_n = 6.6 \times 10^3$ g mol^{-1}, 20 methyl branches and 17 ethyl branches/1000 carbon atoms) are reduced to T_m 86 °C and ca. 25%, respectively.

Table 3. Nonaqueous Ethylene−Norbornene Copolymerization[e]

entry	catalyst	ethylene pressure [bar]	x_{NB} comonomer in solution	X_{NB} in polymer [mol %]	yield [g]	TOF[d] [TO h^{-1}]	M_n[a] [10^3 g mol^{-1}]	M_w/M_n	T_m [°C]	cryst[c] [%]	branches per 1000 C[b]
1−9	**1c**	40			21.6	39 000	61	3.4	125	65	8
3−1	**1c**	40	0.008	0.04	16.4	14 630	51	3.5	125	56	8
3−2	**1c**	40	0.017	0.2	10.0	8880	32	3.4	120	51	9
3−3	**1c**	40	0.025	0.4	9.7	8590	31	3.5	119	46	8
3−4	**1c**	40	0.033	0.5	9.4	8300	31	3.3	118	49	9
3−5	**1c**	40	0.078	1.5	6.4	5510	16	2.4	111	41	9
3−6	**1c**	40	0.145	3.2	6.7	5550	15	2.2	101	29	9
3−7	**1c**	40	0.266	6.0	2.1	1640	14	1.9	85	13	8
1−6	**1b**	40			17.5	31 000	20	2.3	111	45	16
3−8	**1b**	40	0.145	4.9	1.8	1440	17	2.0	65	17	13
3−9	**1b**	20	0.266	8.6	1.0	730	15	2.1	85	6	13
3−10	**2**	40	0.145	4.0	7.0	5700	33	2.0	96	25	10
3−11	**2**	20	0.266	7.6	4.2	3170	29	2.0	77	14	4
1−3	**1a**	40			24.0	43 000	1	2.1			73
3−12	**1a**	40	0.145	4.6	5.7	4580	2	2.1			56
3−13	**1a**	20	0.266	8.1	1.3	960	1	1.6	−42	n.d.	55

[a] Determined by GPC vs linear polyethylene standards. [b] From ^{13}C NMR, branches formed from ethylene monomer only; predominantly Me branches. [c] From DSC. [d] TOF = average turnover frequency, in mol(olefin converted) mol(Ni)$^{-1}$ h^{-1}. [e] Reaction conditions: 100 mL of total volume of toluene solution of norbornene, 40 μmol of catalyst, temperature = 50 °C, reaction time = 1 h (entries 1−9, 1−6, and 1−3, 0.5 h; entry 3−13, 2 h).

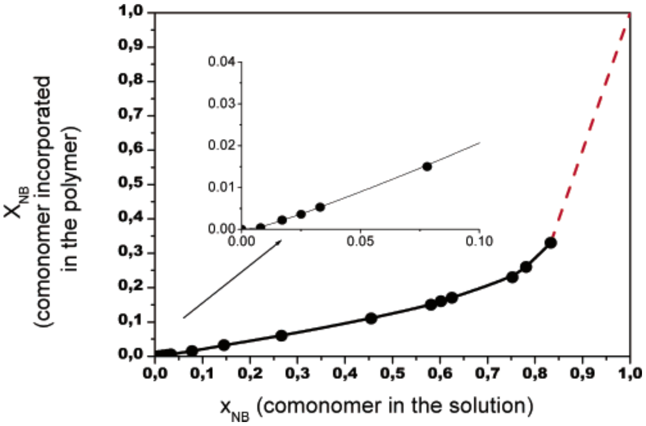


Figure 3. Copolymerization diagram for ethylene−norbornene copolymerization with **1c** at 50 °C.

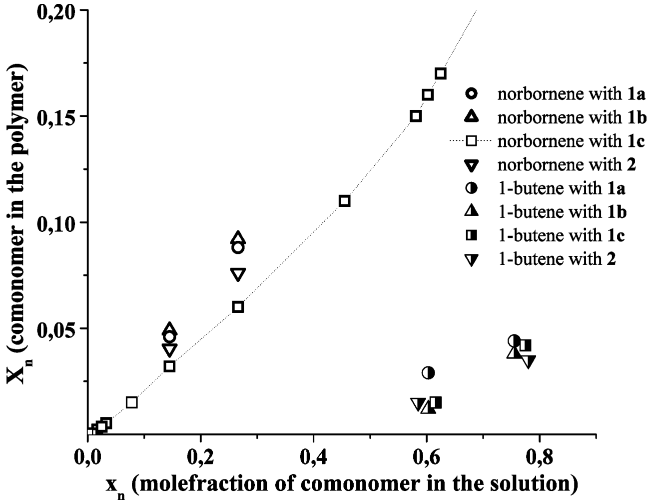


Figure 4. Comparison of ethylene−1-butene and ethylene−norbornene copolymerization with catalyst precursors **1a**−**c** and **2**.

Ethylene—Norbornene Copolymer Latices. In ethylene-1-butene copolymerization, a strong preference for ethylene incorporation limits the amount of comonomer in the polymer at a given composition of the reaction mixture. As noted briefly previously for a polymerization with complex **2**, incorporation of norbornene as a strained cyclic comonomer can be relatively high and the copolymerization is possible in an aqueous system.[4b] The copolymerization of ethylene with norbornene by various nickel(II) and by palladium(II) complexes has been investigated by Rhodes and Goodall,[10] Grubbs,[11] and Kaminsky.[12] Grubbs et al. have reported that salicylaldiminato complexes copolymerize ethylene with norbornene in nonaqueous systems, and copolymers with up to 12 mol % comonomer content were formed.[11] Recently, Lee et al. reported copolymerization of ethylene and norbornene with binuclear salicylaldiminato complexes in nonaqueous media.[13a]

Copolymerization in Nonaqueous Single Phase. The copolymerization behavior of complexes **1a**−**c** and **2** was studied in nonaqueous polymerizations in toluene as a reaction medium (Table 3). The copolymerization was studied in detail for complex **1c**. The full copolymerization diagram is depicted in Figure 3. Please note that the catalyst precursor was found inactive toward norbornene in the absence of ethylene (50 °C; c_{NB} = 0.52 mol L^{-1}); the relationship $X_{NB} = 1$ for $x_{NB} = 1$ given in the diagram is merely a logical assumption.

In the range experimentally investigated, up to $x_{NB} = 0.85$, no azeotrops are observed and incorporation of ethylene prevails. In the range up to $x_{NB} = 0.5$, the molar incorporation of norbornene in the polymer can be approximated by a linear relationship $X_{NB} \approx 0.23x_{NB}$; that is relative incorporation of ethylene prevails ca. 4-fold. The substitution pattern of the catalyst has a certain, limited effect on the relative incorporation. By comparison to **1c**, with **1a** and **1b** relative norbornene incorporation is slightly higher (Table 3 and Figure 4). Comparing these 2,6-aryl substituted catalysts with the 2,6-isopropyl-substituted **2**, incorporations with the latter are intermediate to **1a**−**c**.

The average catalyst activities are lowered by comparison to ethylene homopolymerization and decrease with increasing norbornene content of the reaction mixture and corresponding increase in norbornene incorporation for all four catalyst precursors studied. This is in accordance to the findings of Grubbs et al. for polymerization with similar complexes.[11] The question remains whether this behavior is due to a conceivable irreversible catalyst deactivation by the norbornene comonomer or by impurities introduced with the latter, or whether the reaction is slowed with increasing norbornene incorporation. To this end, the reaction was monitored by measuring the ethylene uptake with a mass flow meter. The results clearly show, that the reaction proceeds slower with increasing norbornene content, but that the catalyst stays active for hours.

Table 4. Ethylene−Norbornene Copolymerization in Aqueous Emulsion

entry	NB [g]^c	t [h]	yield [g]	polymer solids content of dispersion [g]	TOF^e [TOh^{-1}]	incorporated NB [mol %]	M_n 10^3 g mol^{-1}	M_w/M_n	branches/1000 C ^{d}	T_m [°C]	cryst. [%]
4−1^a	0.0	1	3.5	3.5	3130	0.0	21	1.8	8	119	50
4−2^a	0.1	1	3.2	3.2	2830	0.5	21	2.1	9	118	47
4−3^a	0.4	4	1.7	1.7	343	4.4	n.d	n.d.	8	97	24
4−4^a	0.4	5	1.9	1.9	306	4.5	n.d	n.d.	9	97	23
4−5^a	0.5	2	1.2	1.2	470	5.8	14	2.1	8	83	10
3−4^b	1.0	1	9.4	-	8300	0.5	31	3.3	9	118	49
3−7^b	5.0	1	2.1	-	1640	6.0	14	1.9	8	85	13

[a] Reaction conditions: in emulsion, 98 mL of water; 0.75 g of SDS; 40 μmol of catalyst precursor **1c**; temperature = 50 °C. [b] Solution polymerization for comparison: 100 mL total volume of toluene solution of norbornene; 40 μmol **1c**; temperature = 50 °C; ethylene pressure = 40 bar. [c] Norbornene in the reaction mixture. [d] Relating to ethylene derived repeat units (predominantly Me branches). [e] TOF = average turnover frequency, in mol(olefin converted) mol(Ni)$^{-1}$ h^{-1}.

Thus, the lowering of polymerization rate can be related to a slow insertion of coordinated bulky norbornene, and/or a slow insertion of ethylene after a norbornene insertion (a double insertion of norbornene appears unlikely in view of the aforementioned inactivity for norbornene homopolymerization; moreover investigations of the polymer microstructure reveal no neighboring norbornene repeat units, vide infra). In lower molecular weight samples, unsaturated end groups can be observed by ^{1}H NMR spectroscopy. Internal end groups $-CH_2-CH{=}CH-CH_2-$ and in some cases a small portion of vinyl end groups $CH_2{=}CH-CH_2$-are observed. The exclusive observation of these end groups based on ethylene repeat units, which are also observed in ethylene homopolymers, gives no indication of additional chain transfer modes in norbornene copolymerization vs ethylene homopolymerization. The apparent molecular weights determined by GPC relative to linear polyethylene standards must be interpreted with some caution, as the change in polymer composition (norbornene content) obviously will influence the hydrodynamic behavior. Nonetheless, it appears evident that molecular weights decrease with increasing norbornene incorporation. This is not necessarily a contradiction to the aforementioned finding that norbornene incorporation does not result in additional chain transfer modes. The slowing down of chain growth and also chain transfer by norbornene incorporation (that is the temporary "dormancy" of a chain associated with each norbornene insertion) may result in increased lifetimes of a growing chain on the order of the duration of the polymerization experiment. While not representing a proof due to the aforementioned necessary caution in interpreting GPC data, the decrease in M_w/M_n with increasing norbornene incorporation and corresponding decrease in overall polymerization rate is in accordance with this assumption.

Copolymerization in Aqueous Emulsion. For the synthesis of polymer latices (Table 4), the catalyst precursor was dissolved in the norbornene monomer containing a small amount of toluene to render the mixture liquid at room temperature (T_m of norbornene: 40 °C), and a small amount of hydrophobe (hexadecane). The mixture was miniemulsified in an aqueous solution of SDS by means of shear generated with ultrasound, and exposed to ethylene pressure in a polymerization reactor at 50 °C. As for ethylene homopolymerization, catalyst activities are reduced in aqueous emulsion by comparison to polymerization in toluene when polymerizations affording polymers of similar composition are regarded (entries 3−4 vs 4−2 and 3−7 vs 4−5). This can again be related to a partial decomposition of the catalyst during the miniemulsion procedure as a possible explanation. Also, like in nonaqueous copolymerizations, the polymerization rate decreases with increasing amount of norbornene in the reaction mixture and correspondingly increased incorporation. Remarkably, following the polymerization over time by means of the ethylene uptake, it is found that the reaction proceeds at a rather low, but steady rate (see Supporting Information). The catalyst is stable in the copolymerization in emulsion for hours.

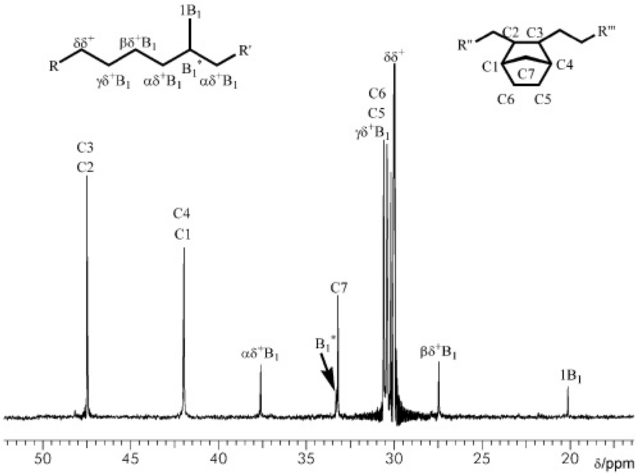


Figure 5. ^{13}C NMR spectrum of an ethylene−norbornene copolymer (entry 3−7 in Table 3; $M_n = 1.4 \times 10^4$ g mol^{-1}; $M_w/M_n = 1.9$; $X_{NB} =$ 6.0 mol %; prepared with catalyst **1c** at 50 °C).

For a given amount of norbornene in the reaction mixture, incorporation and conversion in the aqueous system is much higher that in the nonaqueous copolymerization. In the compartmented multiphase aqueous system, the volume of the organic phase in which the norbornene will be present (initially the miniemulsion droplets, and the amorphous regions of the polymer formed) represents only a fraction of the overall reaction volume. Correspondingly, the local concentration of the comonomer at the (lipophilic) catalytically active sites will be substantially higher. An estimate of the relative comonomer concentration and the incorporation in aqueous emulsion vs the nonaqueous polymerization is consistent (entries 3−4 vs 4−2 and 3−7 vs 4−5). A further, precise quantitative consideration is hampered by the incomplete knowledge of the volume of the organic phase in emulsion containing the norbornene, and much more by losses of small amounts of norbornene which sublime into the reactor head.

Copolymer Microstructure and Properties. Microstructures of the polymers were investigated by high temperature ^{13}C NMR spectroscopy. The spectrum for a copolymer obtained with catalyst precursors **1c** is depicted in Figure 5. Isolated norbornene units are observed exclusively, in addition to the linear polyethylene backbone and some methyl branches. In samples with a norbornene content of up to 30 mol %, some alternating units −E−NB−E−NB−E− are also observed, as expected statistically. Overall, in the range of compositions investigated

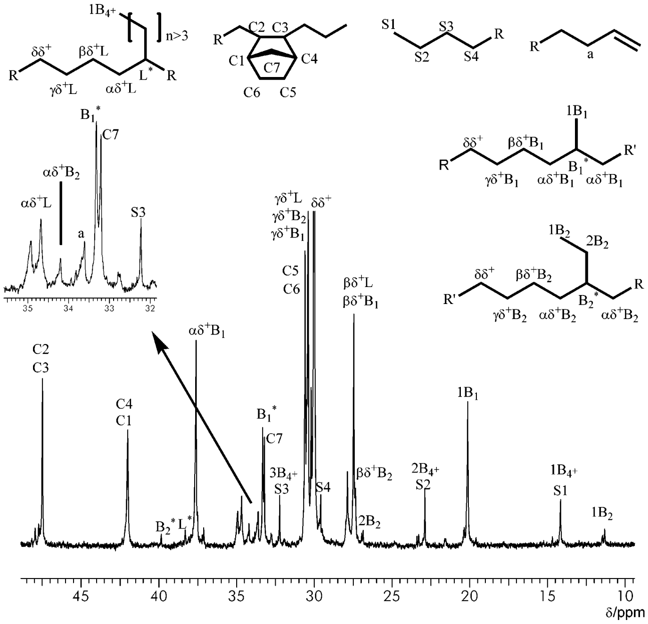


Figure 6. ^{13}C NMR spectrum of a highly branched ethylene−norbornene copolymer (entry 3−13 in Table 3: $M_n = 10^3$ g mol^{-1}; $M_w/M_n = 1.6$; $X_{NB} = 8.1$ mol %; prepared with catalyst **1a** at 50 °C).

no propensity of the catalyst for formation of blocks or alternating structures is observed.

The spectrum for the highly branched copolymer obtained with **1a** is considerably more complex (Figure 6). Signals originating from methyl-, ethyl-, and longer branches (C_{4+}) as well as terminal end groups $-CH_2-CH{=}CH_2$ are observed. In addition, further signals arise from branches in close proximity to one another. For the norbornene units, again only one set of signals arising from isolated units is observed. This also shows that no branches occur on the carbon atoms adjacent to the bulky norbornene repeat units; i.e., the norbornene units are linked to $-CH_2-$ groups. For all copolymers investigated, the degree of branching (calculated relative to the number of carbon atoms originating from ethylene monomer) does not differ significantly from the ethylene homopolymers obtained with the same catalyst under identical reaction conditions (temperature, ethylene pressure).

The thermal properties of linear ethylene-norbornene copolymers prepared by metallocene catalysis have been investigated extensively. Such copolymers are available commercially as transparent, amorphous thermoplastics characterized by a relatively high T_g of about 60−180 °C. For random copolymers, the T_g increases linearly with norbornene content by weight. To achieve the desired properties, norbornene incorporations are usually around 50 wt % or higher. In contrast, our investigations aim at incorporating only low amounts of norbornene sufficient to reduce the crystallinity. Keeping the T_g below room temperature at the same time can be desirable to enable film formation at room temperature. The relationship between copolymer composition and crystallinity and melting point is given for the slightly branched copolymers obtained with catalyst precursor **1c** in Table 4 and depicted in Figure 7. While molecular weights differ between the samples, they are sufficiently high for all samples to not affect the melting behavior and crystallinity to a large extent. Crystallinity decreases approximately linearly with norbornene content as predicted by the Flory equation, in accordance with the findings of Arndt et al. for linear ethylene-norbornene copolymer prepared with metallocene catalysts.[13b] At 14 wt % norbornene content, the material is entirely amorphous, with a T_g of +1 °C (for the partially crystalline polymers with lower norbornene contents glass transitions were to weak for unambiguous observation).

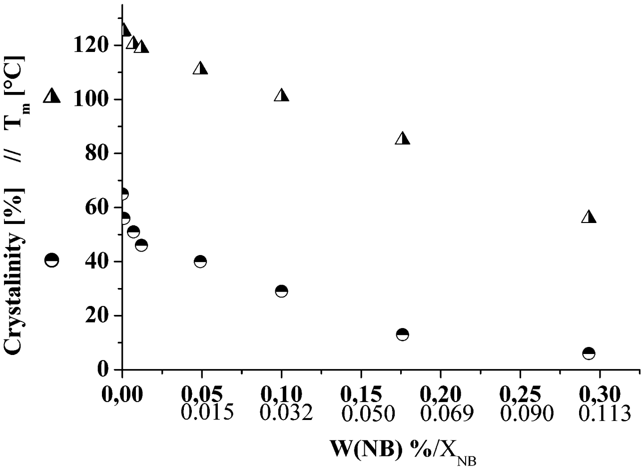


Figure 7. Crystallinity and melt peak vs copolymer composition for ethylene−norbornene copolymers prepared with catalyst **1c** (W_{NB} = weight fraction of norbornene in copolymer).

Polymer Latex Properties. Polymer latices were studied by transmission electron microscopy. Samples were prepared by evaporation of a drop of latex on a grid at room temperature. Concievable residues of norbornene in the particles have no observable effect on the particle behavior: No differences were observed between latices, purified from the excess of SDS and any unreacted comonomer by dialysis, and untreated samples. Particle size distributions are fairly broad with number-average particles sizes of roughly 100 nm. Figure 8 depicts TEM micrographs of latices with varying copolymer composition and crystallinity. In comparison to the sample with 0.5 mol % norbornene content (left), at 2.7 mol % film formation appears to occur already at the periphery of adjacent particles. At 5.5 mol % norbornene content, a continuous featureless film is observed. Correspondingly, on a macroscopic scale evaporating such a dispersion at room temperature a transparent tough film is formed.

Summary and Conclusions

Aqueous dispersions of copolymers with molecular weights $M_n > 10^4$ g mol^{-1} can be prepared with salicylaldiminato-substituted Ni(II) catalysts. For the catalyst precurors studied, polymerization continues for hours also in aqueous emulsion. Polymerization activities are lowered by comparison to ethylene homopolymerization due to slow insertion of 1-butene or norbornene comonomer, respectively. Ethylene is incorporated much more than butene, with the ratio of mole fraction of butene in copolymer/mol fraction of butene in reaction mixture, X_{Bu}/x_{Bu}, being ca. 0.05 under typical reaction conditions. By comparison, the strained olefin norbornene is incorporated much better, typically $X_{NB}/x_{NB} \sim 0.25$. Microstructure analysis by ^{13}C NMR reveals that incorporation of butene occurs in a 1,2- and 1,3-fashion. Very likely 1,4-incorporation also occurs, albeit to a smaller extent, as observed in 1-olefin homopolymerization.[9] Whether 1,2-incorporation (ethyl branches) or 1,3-corporation (methyl branches) prevail depends on the remote substituents of the catalyst precursor employed. Norbornene incorporation effectively reduces crystallinity. For example, with 5 wt % incorporation (1.5 mol %), crystallinity is reduced to 40% vs 65% for the corresponding ethylene homopolymer; at 14 wt % norbornene incorporation the material is entirely amorphous.

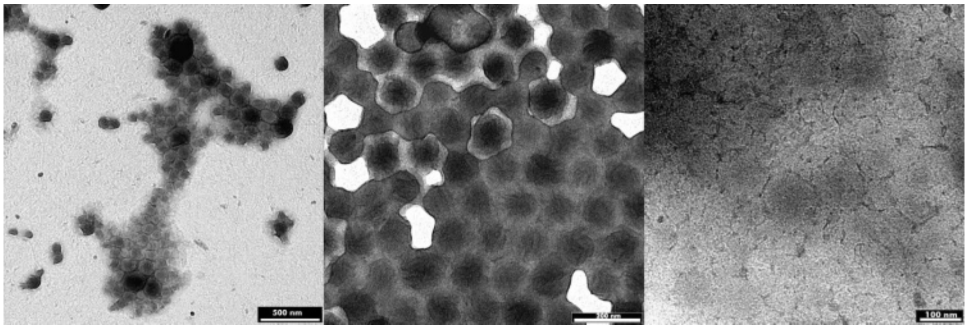


Figure 8. TEM images of ethylene−norbornene latex particles: (left) X_{NB} 0.5%; (middle) X_{NB} 2.7%; (right) X_{NB} 5.8%. Scale bars: left image, 500 nm; middle image, 200 nm; right image, 100 nm).

The glass transition temperature is below room temperature at the same time. Ethylene−norbornene copolymers form tough, flexible films upon evaporation of water from the dispersions.

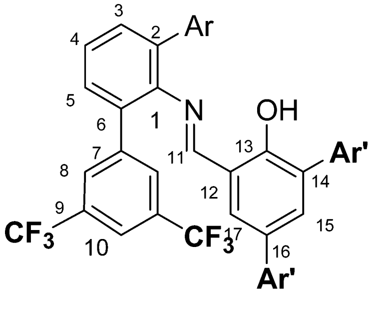
Experimental Section

General Considerations. All manipulations of nickel complexes were carried out under an argon atmosphere (99.999% pure argon supplied by Messer). Toluene and ether were distilled from sodium. Demineralized water was degassed by distillation under argon. Pyridine and pentane were distilled from KOH. Ethylene (purity 99.95%) supplied by Praxair and 1-butene (purity 99.6%) supplied by GHC GmbH were used as received. Norbornene, supplied by Aldrich, was distilled under argon. NMR spectra were recorded at room temperature on a Bruker ARX 300 spectrometer. ^{1}H and ^{13}C NMR spectra of polyethylenes were obtained in 1,1,2,2-tetrachloroethane-d_2 at 122 °C. The branching structure was assigned according to Randall[14] and Wagener.[15] Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC 7 or on a Netzsch F1 DSC at a heating and cooling rate of 10 K min^{-1}. DSC data reported are second heats. Polymer crystallinities were calculated based on a melt enthalpy of 293 J g^{-1} for 100% crystalline polyethylene. GPC analyses were carried out on a Polymer-Laboratories GPC220 instrument equipped with Mixed B columns at 160 °C in 1,2,4-trichlorobenzene. Data are referenced to linear polyethylene standards. Complexes **1a**, **1b**, and **2** were prepared as described previously.[4b,f]

Synthesis of 6-C(H)=N[2,6-{3,5-$(F_3C)_2C_6H_3$}$_2$$C_6H_3$]-2,4-{3,5-$(F_3C)_2C_6H_3$}$_2$$C_6H_2$OH. The corresponding aldehyde, 6-C(H)=O-2,4-{3,5-$(F_3C)_2C_6H_3$}$_2$$C_6H_2$OH, was prepared by Suzuki coupling reacting a solution of 3,5-bis(trifluoromethyl)phenylboronic acid (4.0 g, 15.5 mmol) in EtOH (12 mL), and 3,5-diiodosalicylaldehyde (1.93 g, 5.2 mmol) in toluene (60 mL) in the presence of $Pd(PPh_3)_4$ (5 mol %) and Na_2CO_3 solution (2 M; 24 mL) at 90 °C, overnight.

R_f = 0.76 (Toluene). ^{1}H NMR (400 MHz, $CDCl_3$): 11.74 (s, 1H, OH), 10.11 (s, 1H, C(O)H), 8.08 (br, 2H, CH), 8.01 (br, 2H, CH), 7.93 (br, 1H, CH), 7.91 (br, 1H, CH), 7.90 (m, 1H, CH), 7.82 (m, 1H, CH).

To a solution of the aldehyde (1.27 mmol) in methanol (4 mL), 2,6-bis{3,5-di(trifluoromethyl)phenyl}aniline[4f] (1.16 mmol) and a catalytic amount of formic acid were added and heated overnight to 60 °C. The precipitated imine was isolated by filtration. (Yield: 70%.)



^{1}H NMR (600 MHz, $CDCl_3$): 12.84 (br, 1H, O*H*), 8.20 (s, 1H, N=*H*C), 8.06 (br, 2H, C$H^{Ar'}$), 7.96 (br, 4H, C^8*H*), 7.93 (br, 1H, C$H^{Ar'}$), 7.89 (br, 2H, C^{10}*H*), 7.86 (br, 3H, C$H^{Ar'}$), 7.66 (d, ^4J = 2.3 Hz, 1H, C^{15}*H*), 7.60 (m, 3H, C^3*H*, C^4*H*, C^5*H*), 7.21 (d, ^4J = 2.3 Hz, 1H, C^{17}*H*). ^{13}C NMR (151.2 MHz, $CDCl_3$): 169.3 (N=*C*H), 158.6 (*C*-OH), 144.9 (C^1); 141.3, 140.7, 138.3, 130.1, 128.5, and 127.3 (quaternary C each, C^2, $C,^6$ $C,^7$ $C,^{14}$ $C,^{16}$ $C^{Ar'}$) 133.3 (C^{15}), 132.5, 132.1, and 131.8 (q, ^2J = 33 Hz, *C*CF_3), 131.4 (C^3, C^5), 131.3 (C^{17}), 130.0 (br, C^8), 129.5 (br, *C*$H^{Ar'}$), 127.3 (C^4), 126.7 (br, *C*$H^{Ar'}$); 123.39, 123.22, and 123.10 (q, *J* = 273 Hz, *C*F_3); 121.6, and 121.1 (m, *C*$H^{Ar'}$), 121.4 (m, C^{10}), 118.9 (s, C^{12}); ^{19}F NMR (282.4 MHz, C_6D_6, room temperature): −62.9 (CF_3).

Complex 1b was prepared in analogy to literature procedures.[4b,f] To an ether (10 mL) solution of $[(tmeda)Ni(CH_3)_2]$[16] (100 mg, 0.49 mmol; supplied by MCAT, Konstanz) was added 0.49 mmol of the salicylaldimine ligand at −30 °C, followed by 0.5 mL of pyridine. The temperature was raised to 0 °C, and the orange-red mixture was stirred for 2 h. The solvent was removed in vacuo and the residue was washed with cold pentane.

^{1}H NMR (400 MHz, C_6D_6): 8.21 (s, 4H), 7.88 (br, 2H, py), 7.80 (s, 2H), 7.70 (s, 3H), 7.58 (s, 1H), 7.55 (s, 2H), 7.05 (d, ^4J = 2.3 Hz, 1H), 7.01−6.91 (m, 3H), 6.89 (s, 1H), 6.71 (d, ^4J = 2.3 Hz, 1H), 6.55 (br, 1H, py), 6.13 (br, 2H, py), −0.90 (s, 3H, Ni−Me). ^{13}C NMR (100.5 MHz, C_6D_6): 168.4, 164.8, 150.4 (br, py), 150.3, 142.6, 141.6, 141.5, 136.7, 133.4, 133.2, 132.3, and 132.1 (q, ^2J = 33 Hz, *C*CF_3), 131.7, 130.9, 129.4, 127.0, 126.0, 125.9, 125.8, 124.0, 124.0, and 123.7 (*q J* = 273 Hz, *C*F_3) 121.6, 120.2, 120.0, 119.9, −7.2 (Ni−Me). Anal. Calcd (%) for $NiC_{51}H_{26}F_{24}N_2O$ (1197.4): C, 51.16; H, 2.18; N, 2.34; Found: C, 49.57; H, 1.98; N, 2.34. This deviation is likely due to high fluorine content which disturbs elemental analysis.

Ethylene copolymerization in nonaqueous media was carried out in a 300 mL stainless steel mechanically stirred (1000 rpm) pressure reactor equipped with a heating/cooling jacket supplied by a thermostat controlled by a thermocouple dipping into the polymerization mixture.

In experiments with 1-butene, the comonomer was condensed in a glass flask at −70 °C, and transferred to the precooled pressure reactor at −20 °C. Then the pressure reactor was charged with a solution of 40 μmol of complex (**1a**−**c** or **2**) in toluene up to 100 mL total volume. In the case of norbornene as the comonomer, the pressure reactor was charged with a solution of 40 μmol of complex in 100 mL of toluene/norbornene mixture.

The pressure reactor was flushed with ethylene, and a constant ethylene pressure was then applied and the reaction mixture was brought rapidly to the desired temperature. After a specified reaction time, the reactor was rapidly vented and cooled. The polymerization mixture was poured into a 3-fold volume of methanol to precipitate any dissolved low molecular weight material. The polymer was isolated by filtration, washed three times with methanol, and dried in vacuo.

Ethylene/Norbornene Copolymerization in Aqueous Emulsion. In a Schlenk tube, a solution of catalyst precursor (**1a**−**c** or **2**) in a mixture of toluene (2 mL), hexadecane (0.3 mL), and norbornene was added to an aqueous (98 mL of water) solution of

0.75 g of sodium dodecyl sulfate (SDS). The mixture was homogenized under an argon atmosphere by means of an ultrasonic homogenizer (Bandelin HD2200 with KE76 tip, operated at 120 W, 2 min). The resulting miniemulsion was cannula-transferred to the aforementioned 300 mL pressure reactor. The pressure reactor was flushed with ethylene, and a constant ethylene pressure was then applied and the reaction mixture was brought rapidly to the desired temperature. After the specified reaction time, the reactor was vented and cooled. The emulsion was filtered through glass wool to separate any coagulate and to determine its amount. For determination of yields and for further polymer analysis a specified portion of the latex was precipitated by pouring into excess methanol. The polymer was washed three times with methanol and dried in vacuo.

Ethylene/Butene Copolymerization in Aqueous Emulsion. A measured amount of 1-butene was condensed into the aforementioned 300 mL pressure reactor at −20 °C. After the reactor was heated to the desired reaction temperature, approximately 80 mL of a solution of 0.75 g of SDS in 98 mL of water was added by a pump. The reaction mixture was pressurized with ethylene (10 bar) and stirred for 15 min. In a Schlenk tube, a solution of catalyst precursor (**1a**−**c** or **2**) in a mixture of toluene (2 mL) and hexadecane (0.3 mL) was added to the remaining portion of aqueous SDS solution (ca. 18 mL). The mixture was homogenized under an argon atmosphere by means of an ultrasonic homogenizer (Bandelin HD2200 with KE76 tip, operated at 120 W, 2 min). The resulting miniemulsion was transferred to the pressure reactor by a pump. The ethylene pressure in the pressure reactor was raised to 40 bar while the reaction mixture was brought rapidly to the desired temperature. After the specified reaction time, the reactor was vented and cooled. The emulsion was worked up as described above.

Acknowledgment. Financial support by BASF AG is gratefully acknowledged. S.M. is in debt to the Fonds der chemischen Industrie and the Hermann Schnell-foundation for financial support. We thank Christine Stoz for her participation in part of this research during her undergraduate studies.

Supporting Information Available: Figures S1−S5 showing mass flow diagrams and GPC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA060813T