Influence of *n*-Alkyl Branches on Glass-Transition Temperatures of Branched Polyethylenes Prepared by Means of Metallocene- and Palladium-Based Catalysts

Dietmar Mäder, Johannes Heinemann, Philipp Walter, and Rolf Mülhaupt*

Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie der
Albert-Ludwigs-Universität, Stefan-Meier-Strasse 31, D-79104 Freiburg i. Br., Germany

Received July 7, 1999

ABSTRACT: Branched polyethylenes with controlled molecular architectures were prepared by means of metallocene-catalyzed copolymerization of ethylene with 1-olefins such as propylene, 1-butene, 1-hexene, and 1-octene and by means of migratory-insertion-type ethylene homopolymerization using methylpalladium diazadiene borate as catalyst. Glass-transition temperatures, T_g, as determined by means of dynamic mechanical analysis (DMA), were correlated with propylene and 1-butene weight fractions of ethylene copolymers over the entire composition range. Several correlations between degree of branching and T_g were evaluated for ethylene-rich copolymers and branched ethylene homopolymers. The conventional degree of branching is defined as the number of branched tertiary C atoms per 1000 C atoms of the methylene units or 1000 C atoms of the entire polymer chain. We propose a new degree of branching that is defined as sum of the number of branched tertiary C atoms in the polyethylene chain and the C atoms of the *n*-alkyl branch, referred to 1000 C atoms of the polyethylene backbone, that gives excellent correlation with T_g of branched polyethylene, independent of the branch type and the synthetic route used to prepare branched polyethylene.

Introduction

Recent innovations in transition-metal-catalyzed low-pressure ethylene polymerization give excellent control of polyolefin molecular architectures. Such tailor-made polyolefins represent attractive model systems to establish basic correlations between catalyst and polymer structures as well as polymer properties. Branched polyethylene model polymers with controlled degree of branching can be prepared via group 4 metallocene-catalyzed ethylene copolymerization with 1-olefins or by means of migratory insertion ethylene homopolymerization using group 10 diazadiene complexes as catalysts. In contrast to conventional multisite catalysts, which gave rather complex mixtures of branched polyethylene with molar mass-dependent degree of branching, modern single-site catalysts produce very uniform copolymers with narrow molar mass distribution ($M_w/M_n \approx 2$) and molar mass-independent uniform comonomer incorporation.[1] The range of tailor-made ethylene/1-olefin copolymers includes linear low-density polyethylene (LLDPE), linear polyethylene with very low density (VLDPE), highly flexible thermoplastic elastomers, also referred to as plastomers, and rubbers.[2−4] Metallocene-catalyzed copolymerizations of ethylene with propylene,[5,6] 1-butene,[7,8] 1-hexene,[9] and 1-octene[9−12] have been reported. Today, there exists profound knowledge on the influences of comonomer incorporation and stereochemical irregularities on melting temperature and crystallization behavior.[13] However, much less is known about the influence of branching on glass-transition temperature, T_g. Prior to the metallocene age, model polymers such as hydrogenated poly(1-methyloctamer) were designed to examine thermal properties of EPM rubber as a function of comonomer incorporation.[14] Hydrogenated butadiene copolymers[15] and, recently, hydrogenated butadiene terpolymers were proposed as model systems for branched polyethylenes.[16] Due to other sequence distribution,[17] especially when considering high olefin content, such model systems are only useful in rather narrow ranges of comonomer incorporation.

Another route to branched polyethylene represents migratory insertion homopolymerization that does not require comonomer addition to introduce alkyl branches into the polyethylene chain. During ethylene polymerization, group 10 metal alkyls can migrate along the polyethylene chain via repeated sequences of β-hydrid elimination followed by reinsertion. This mechanism was referred to as 2,ω-polymerization by Möhring and Fink[18] and chain walking by Brookhart et al.[19] When polymerization occurs exclusively at the polyethylene chain end, 2,ω-polymerization affords methyl-branched polyethylenes. When insertion takes places also during migration along the polyethylene chain, as observed for palladium diazadiene-based catalysts,[19] highly branched amorphous polyethylene is obtained. In Ni-catalyzed polymerization, the degree of branching decreases with increasing ethylene pressure. In contrast, Pd-catalyzed ethylene homopolymerization produced highly branched polyethylene where branching is independent of ethylene pressure.[20] Both group 4 and 10 catalyst families give control of polyethylene branching via the molecular architectures of the catalysts.

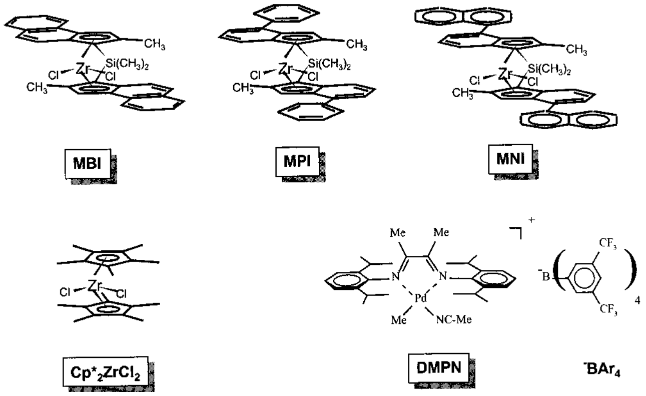
The possibility of controlling the degree of short chain branching via migratory insertion or 1-olefin incorporation without sacrificing narrow molar mass distribution and uniform branching distribution offers attractive potential for better understanding of basic correlations between catalyst and polymer structures as well as polymer properties such as glass-transition temperature (T_g). Metallocene-based ethylene copolymers are excellent model systems to understand the influence of polyethylene molecular architectures on glass-transition

---

* Fax: (++49) 761/203-6319. E-mail: mulhaupt@fmf.uni-freiburg.de.

10.1021/ma991096o CCC: $19.00

Scheme 1. Catalyst Components MBI, MPI, MNI, $Cp^*_2ZrCl_2$ and DMPN/Borate



temperatures. An important objective of this research is to examine how number and length of the *n*-alkyl branches influence the T_g of branched polyethylenes and how the synthetic method affects this correlation.

Experimental Section

Materials. Synthesis of poly(ethylene-*co*-propylene) (EP),[6] poly(ethylene-*co*-1-butene) (EB),[8] poly(ethylene-*co*-1-hexene) (EH),[9] and poly(ethylene-*co*-1-octene) (EO)[11] is performed using methylaluminoxane (MAO)-activated *rac*-dimethylsilylenebis-(2-methylbenz[*e*]indenyl)zirconium dichloride (MBI) (displayed in Scheme 1) following procedures that are described elsewhere.[11] To exclude influences of catalyst residues, all copolymers are extracted with boiling xylene for 24 h, prior to use. In polymer samples, code numbers behind the copolymer abbreviations denote the comonomer content in weight percent. EB10 (Luflexen HS0322) is supplied by BASF AG, EB24 (Tafmer A4085) is supplied from Mitsui, EO19 (Exact 2 M011) is provided from Dex Plastomers, and EO25 (Engage 8150) is from Dow Chemical. Metallocene-based polyethylene (HDPE) is kindly provided from Dr. U. Rief (BASF AG). Highly branched polyethylenes, brPE, are prepared from *N,N′*-[bis-(2,6,-diisopropylphenyl)-1,4,-diaza-2,3-dimethyl-1,3-butadiene]-acetonitrilo-methylpalladium (tetra(3,5-bis(trifluormethyl)-phenyl)borate), abbreviated DMPN/borate, as described in detail elsewhere.[20] brPE contains branches equivalent to propylene and 1-butene incorporation and branches corresponding to 1-pentene, 1-hexene, and 1-octene, and so on, if brPE is considered as an ethylene copolymer.

The molar masses and molar mass distributions are determined by size exclusion chromatography (SEC) in 1,3,5-trichlorobenzene at 135 °C, calibrated against polyethylene standards. Physical properties of the polymers are listed in Tables 1−4. The melting points and melting enthalpies of the poly(ethylene-*co*-1-octene) are listed elsewhere.[11]

Table 1. MBI/MAO-Catalyzed Ethylene/Propylene Copolymers (EP)

polymer[a] sample propylene cont. (wt %)	HDPE PW001 0	EP11 JS75 11	EP17 JS74 17	EP38 PW055 38	EP46 PW023 46	EP50 JS85 50	EP61 JS60 61	EP75 PW022 75	EP84 JS77 84	EP95 JS78 95	*i*-PP N4 100
$[E]_{polym}$ (mol %)[b]	100	92.5	87.7	71.2	64.0	59.6	49.0	33.8	22.9	8.0	0
$[P]_{polym}$ (mol %)[b]	0	7.5	12.3	28.8	36.0	40.4	51.0	66.2	77.1	92.0	100
$[E]_{polym}$ (wt %)[b]	100	89.2	82.6	62.2	54.3	49.6	39.0	24.4	16.5	5.5	0
$[P]_{polym}$ (wt %)[b]	0	10.8	17.4	37.8	45.7	50.4	61.0	74.6	83.5	94.5	100
M_n (kg/mol)[c]	282.8	143.6	152.0	45.7	28.3	39.9	21.4	38.4	49.6	96.9	117.0
M_w/M_n[c]	3.5	1.9	1.7	2.1	2.2	2.2	2.2	2.1	1.9	1.5	2.2
T_g (°C) from DMA[d]	broad (−25)	−26.0	−28.2	−43.2	−45.6	−47.6	−46.5	−32.2	−17.5	−4.5	6.3
maximum of E''	−28.1	−30.2	−39.4	−48.7	−50.2	−51.7	−50.2	−36.3	−23.7	−11.7	1.1
T_g (°C) from DSC[e]	[f]	−28.8	−31.2	−37.1	−49.5	−50.6	−49.6	−35.1	−27.1	−13.6	−2.0
T_m (°C)[e]	136.5	106.3	71.5	[f]	[f]	[f]	[f]	[f]	81.6	116.5	149.5
ΔH_m (J/g)[e]	182.0	104.4	61.0	[f]	[f]	[f]	[f]	[f]	10.6	45.8	84.5
T_{cr}[e]	113.5	72.3	54.3	[f]	[f]	[f]	[f]	[f]	32.4	72.3	113
DB (eq 4)	0	36	58	126	153	168					
DB* (eq 11)	0	75	123	288	360	404					

[a] Polymer sample code numbers behind the copolymer abbreviations denote the comonomer content in weight percent. [b] Determined by means of ^{13}C NMR. [c] Determined by means of SEC (1,3,5-trichlorobenzene at 135 °C, PE standard). [d] Determined by means of dynamic mechanical analysis at a heating rate of 2 K/min as maximum of tan(δ). [e] Determined by means of DSC at a heating/cooling rate of 10 K/min. [f] Not detectable.

Table 2. MBI/MAO-Catalyzed Ethylene/1-Butene Copolymers (EB)

polymer[a] sample 1-butene cont. (wt %)	HDPE PW001 0	EB10 HS0322 10	EB24 A4085 24	EB32 AK7 32	EB48 JS81b 48	EB52 AK5 52	EB58 PW12−2 58	EB62 JS84 62	EB70 AK9 70	EB82 JS80a 82	EB90 JS83b 90	*i*-PB JS19 100
$[E]_{polym}$ (mol %)[b]	100	94.6	86.7	80.9	68.9	64.7	58.8	54.1	43.9	30.1	19.0	0
$[B]_{polym}$ (mol %)[b]	0	5.4	13.3	19.1	31.1	35.3	41.2	44.9	56.1	69.9	81.0	100
$[E]_{polym}$ (wt %)[b]	100	89.7	76.4	67.8	52.1	47.8	41.7	38.0	30.4	17.7	10.5	0
$[B]_{polym}$ (wt %)[b]	0	10.3	23.6	32.2	47.9	52.2	58.3	62.0	69.9	82.3	89.5	100
M_n (kg/mol)[c]	282.8	52.0	55.4	107.9	60.8	82.8	48.2	65.6	62.4	40.5	73.9	46.7
M_w/M_n[c]	3.5	2.3	2.3	2.3	2.2	2.4	2.7	2.2	2.4	2.2	2.2	2.8
T_g (°C) from DMA[d]	broad (−25)	broad	−33	−37	−54	−55.1	−56	−52	−44.4	−32	−27	−15.2
maximum of E''	−28.1	−32	−43	−47	−61	−61.1	−62	−56.9	−51.3	−40.3	−34	−23.1
T_g (°C) from DSC[e]	[f]	−29.7	−35.2	−41.2	−60.1	−60.4	−60.5	−57.1	−52.2	−41.9	−37.7	−25.4
T_m (°C)[e]	136.5	98.7	74.4	55.3	[f]	[f]	[f]	[f]	[f]	41.2	56.7	97.7
ΔH_m (J/g)[e]	182.0	82.2	74.5	50.3	[f]	[f]	[f]	[f]	[f]	15.5	26.7	30.7
T_{cr}[e]	113.5	82.4	67.3	[f]	[f]	[f]	[f]	[f]	[f]	[f]	[f]	81.0
DB (eq 4)	0	26	61	80	119	130	146					
DB* (eq 11)	0	81	207	287	467	530	618					

[a] Polymer sample code numbers behind the copolymer abbreviations denote the comonomer content in weight percent. [b] Determined by means of ^1H NMR. [c] Determined by means of SEC (1,3,5-trichlorobenzene at 135 °C, PE standard). [d] Determined by means of dynamic mechanical analysis at a heating rate of 2 K/min as maximum of tan(θ). [e] Determined by means of DSC at a heating/cooling rate of 10 K/min. [f] Not detectable.

Table 3. MBI/MAO-Catalyzed Ethylene/1-Hexene (EH) and Ethylene/1-Octene Copolymers (EO)

polymer[a]	sample	1-alkene X	$[E]_{polym}$ (mol %)[b]	$[X]_{polym}$ (mol %)[b]	$[E]_{polym}$ (wt %)[b]	$[X]_{polym}$ (wt %)[b]	M_n (kg/mol)[c]	M_w/M_n[c]	DB (eq 4)	DB* (eq 11)	T_g (°C) DMA[d]	max of E'' [c]	T_g (°C) DSC[e]
EH15	JH192	H	94.3	5.7	84.7	15.3	126.9	2.4	26	143	−27.0	−38.8	−36.7
EH28	JH208	H	88.4	11.6	71.8	28.2	96.5	2.3	47	290	−39.6	−48.4	−42.8
EH36	JH191	H	84.1	15.9	63.8	36.2	85.2	2.4	60	398	−44.6	−53.0	−38.0
EH42	JH177	H	80.7	19.3	58.2	41.8	81.5	2.7	70	483	−47.9	−54.9	−54.8
EH72	JH205	H	54.1	45.9	28.2	71.8	66.3	2.5			−52.3	−57.6	−56.3
i-PH	JH174	H	0	100	0	100	20.4	6.9			−27.6	−38.3	−43.8
EO19	2M011	O	94.5	5.5	81.0	19.0	42.8	2.6	24	194	−35.8	−46.6	−40.7
EO25	EG8150	O	92.3	7.7	75.0	25.0	77.2	2.1	32	270	−42.9	−51.5	−49.3
EO31	JH150	O	89.8	10.2	60.6	31.2	107.6	2.6	39	357	−45.9	−55.1	−53.2
EO48	JH122	O	82.2	17.8	52.3	47.7	82.1	2.9	58	616	−54.2	−61.6	−62.1
EO63	PW58	O	70.6	29.4	37.5	62.5	131.0	2.4	78	1029	−57.0	−64.6	−64.1
EO66	JH188	O	67.6	32.4	34.3	65.7	71.9	2.2	82	1134	−57.7	−65.0	−67.2
i-PO	JH181	O	0	100	0	100	20.0	5.3			−52.1	−63.4	−66.5

[a] Polymer sample code numbers behind the copolymer abbreviations denote the comonomer content in weight percent. [b] Determined by means of ^{1}H NMR and ^{13}C NMR. [c] Determined by means of SEC (1,3,5-trichlorobenzene at 135 °C, PE standard). [d] Determined by means of dynamic mechanical analysis at a heating rate of 2 K/min as maximum of tan(θ). [e] Determined by means of DSC at a heating rate of 10 K/min.

Table 4. Highly Branched Polyethylenes (brPE) As Prepared by Palladium Catalysis (DMPN/Borate)

polymer	sample	1-alkene	$[E]_{polym}$ (mol %)[a]	$[X]_{polym}$ (mol %)[a]	$[E]_{polym}$ (wt %)[a]	$[X]_{polym}$ (wt %)[a]	M_n (kg/mol)[b]	M_w/M_n[b]	DB (eq 4)	DB* (eq 11)	T_g (°C) DMA[c]	max of E'' [c]	T_g (°C) DSC[d]
brPE53	JH53	P	69.7	9.9	46.6	9.9	171.0	1.8	102	645	−54.6	−59.8	−62.0
		B		6.9		9.2							
		Pen		0.6		1.0							
		Hex		2.4		4.8							
		Hep		0.9		2.1							
		O, etc.		9.9		26.4							
brPE57	JH41	P	66.1	11.7	42.9	11.4	184.3	2.0	110	710	−57.2	−62.2	−66.5
		B		7.1		9.2							
		Pen		0.6		1.0							
		Hex		2.8		5.4							
		Hep		0.9		2.1							
		O, etc.		10.8		28.0							

[a] Determined by means of ^{13}C NMR. [b] Determined by means of SEC (1,3,5-trichlorobenzene at 135 °C, PE standard). [c] Determined by means of dynamic mechanical analysis at a heating rate of 2 K/min as maximum of tan(θ). [d] Determined by means of DSC at a heating rate of 10 K/min.

NMR Spectroscopy. Polymer sample (30−50 mg) is dissolved in $C_2D_2Cl_4$ at 400 K, and ^{1}H NMR spectra are recorded on a Bruker ARX 300 spectrometer at 300 MHz and ^{13}C NMR spectra at 75.4 MHz. The propylene content in EP and the 1-octene content in EO is determined from ^{13}C NMR analysis. The 1-butene content in EB and 1-hexene content in EH is determined from ^{1}H NMR analysis. The number of individual alkyl branches of highly branched polyethylene brPE, obtained with Pd catalysts DMPN, is determined from ^{1}H NMR and ^{13}C NMR analysis as described in the literature.[21]

Dynamic Mechanical Analysis (DMA). T_g is measured by dynamic mechanical analysis on a Rheometrics Solids analyzer RSA II at 1 Hz and a heating rate of 2 K/min using a dual cantilever geometry (50 × 6 × 2 mm^3) and applying a strain of 0.2%. (Palladium-based highly branched polyethylenes, brPE, are investigated using parallel plate geometry (4.75 mm in diameter, 1 mm thickness) and applying a strain of 0.5%). The storage (E') and loss moduli (E'') and the loss tangent (tan(δ)) are measured from −100 °C up to temperatures accessible with the respective geometry. To show the accuracy of T_g determination by means of DMA, the same sample is measured five times. The maximum of the loss factor/temperature curves is used to determine T_g. The temperature at the maximum of tan(δ) and of the maximum of E'' is listed in Table 1−4. The detected T_g's are within the range of 2 °C; i.e., the accuracy of the T_g determination via DMA is about ±1 °C.

Thermal Analysis. Differential scanning calorimetry (DSC) measurements are performed on a Perkin-Elmer DSC-7 from samples that are crystallized at a cooling rate of 0.1 K/min. EP and EB melting temperatures (T_m), and melting enthalpies (ΔH_m) are taken from the first heating run at a heating rate of 10 K/min and crystallization temperatures (T_{cr}) are determined at a cooling rate of 10 K/min. The T_g is determined from the second heating run at a heating rate of 10 K/min. The accuracy of the determination of T_g via DSC is about ±5 K/min.

Degree of Branching. The various equations applied to calculate the degree of branching are summarized in Table 6.

Results and Discussion

Preparation of Branched Polyethylenes. Branched polyethylenes are prepared by means of MAO-activated MBI-catalyzed copolymerization of ethylene with various 1-olefins such as propylene, 1-butene, 1-hexene, and 1-octene. The copolymerization reactions are performed varying the 1-olefin content in the feed from 0 to 100 wt %. It is well-established that the metallocene structure, especially ligand framework, represents the key to controlled ethylene copolymerization with 1-olefins. The structures of different metallocenes are listed in Scheme 1. For instance, in ethylene/propylene copolymerization, 4-substitution with phenyl (*rac*-dimethylsilylenebis(2-methyl-4-phenylindenyl)zirconium dichloride, MPI) and especially naphthyl (*rac*-dimethylsilylenebis(2-methyl-4-naphthylindenyl)zirconium dichloride, MNI) accounts for significantly improved propylene incorporation with respect to MBI without sacrificing high molar mass and narrow polydispersity (see Table 5). The 1-olefin incorporation is improved in the order MBI < MPI < MNI.[25,26] In fact, catalyst activity of MNI is 1 order of magnitude higher with respect to that of MBI. In comparison to bispentamethylcyclopentadienyl zirconium dichloride ($Cp^*_2ZrCl_2$), the copolymerization parameter for ethylene/propylene copolymerization can be varied by 2 orders of magnitude from $r_E = 256$ for

Table 5. Metallocene-Catalyzed Ethylene/Propylene Polymerization

metallocene run no.[a]	MBI 1	MPI 2	MNI 3	$Cp*_2ZrCl_2$ 4
$[E]_{polym}$ (mol %)[b]	49.1	40.8	25.6	97.9
$[P]_{polym}$ (mol %)[b]	50.9	59.2	74.4	2.1
$[E]_{polym}$ (wt %)[b]	39.2	31.5	18.6	96.9
$[P]_{polym}$ (wt %)[b]	60.8	68.5	81.4	3.1
r_E[c]	5.01	3.27	2.44	256.00
r_P[c]	0.39	0.59	1.26	0.21
r_Er_P	1.9	1.9	3.1	55.4
activity[d]	22 200	113 500	152 000	40 000
M_n [kg/mol][e]	91.9	32.0	44.5	17.0
M_w/M_n[e]	1.5	2.0	2.3	1.9

[a] p_E = 2 bar; [E] = 0.12 mol/L = 24 mol %; [P] = 0.39 mol/L = 76 mol %; 40 °C; solvent, toluene. Run 1 [Zr] = 2 μmol/L, run 2 [Zr] = 0.375 μmol/L, run 3 [Zr] = 1.0 μmol/L, run 4 [Zr] = 3 μmol/L; run 1 Al/Zr = 10 000, run 2 & 3 Al/Zr = 30 000, run 4 Al/Zr = 20 000. [b] Determined by means of ^{13}C NMR. [c] Determined by Uozomi–Soga equation.[28] [d] In [$kg_{polymer}/mol_{Zr}$ h]. [e] Determined by means of SEC (1,3,5-trichlorobenzene at 135 °C, PE standard).

$Cp*_2ZrCl_2$ to $r_E = 2.4$ for MNI. Random ethylene/1-olefin copolymers covering the entire copolymer composition range including the pure poly(1-olefin)s without losing high stereo- and regioselectivity at high 1-olefin contents can be prepared. In contrast, most traditional catalysts and most half-sandwich complexes fail to produce 1-olefin homopolymers and give substantial regioirregularities, as evidenced by head-to-head 1-olefin incorporation.

Nowadays, highly branched polyethylenes containing predominantly methyl, ethyl, and hexyl (or longer) branches can also be synthesized via ethylene homopolymerization using palladium–diimine catalysts, e.g., DMPN/borate. In the following discussion, these *n*-alkyl branches are also considered as short chain branches and will be compared to the classical metallocene-based ethylene copolymers where *n*-alkyl branches are introduced by copolymerization with 1-olefins of different length.

Thermal Properties. Physical properties, including T_g's, of EP are listed in Table 1, those of EB are in Table 2, those of EH and EO are in Table 3, and those of brPE containing methyl, ethyl, propyl, and so on side chains are in Table 4. In sample codes, the number associated with the type of copolymer represents the weight fraction of the 1-olefin incorporated in the copolymer; e.g., "EH28" is a poly(ethylene-*co*-1-hexene) containing 28 wt % 1-hexene. The determination of T_g is performed by means of DMA due to the higher accuracy compared with DSC.[22]

Poly(ethylene-*co*-propylene)s. Typical DMA traces for EP are displayed in Figure 1. Partially crystalline HDPE and ethylene-rich copolymers show rather broad loss factor curves with only small height of the tan(δ) curve (lines a and b in Figure 1). For linear polyethylene, i.e., HDPE, the T_g is assigned to −25 °C as maximum of tan(δ) (line a in Figure 1). In the literature, T_g's for polyethylene are reported in the range between about −130 and +70 °C, with the most frequent quotations centered around −120 and −23 °C, respectively.[23] Figure 1 shows that the T_g of EP copolymers decrease with increasing propylene content ($P \leq 50$ wt %); i.e., the maximum of tan(δ) is shifting to lower temperatures with respect to HDPE. The height of the tan(δ) curve accounts for the degree of crystallinity or amorphous fraction of the copolymer. According to WAXS and DSC, EP17 still exhibits residual crystallinity and a higher maximum of tan(δ) compared to HDPE, thus indicating decreased crystallinity. Short chain branches disturb crystallization of the PE backbone and cause reduced lamellae thickness. This leads to a decrease of the melting temperature of branched PE such as EP with respect to that of linear HDPE. As ethylene sequence length decreases, crystallization is entirely suppressed and the copolymers are rendered amorphous. Consequently propylene-rich copolymers exhibit high values of tan(δ) because there is no residual crystallinity. These findings are confirmed by the absence of any peaks in WAXS and the absence of a melting temperature in DSC measurements. The lowest T_g, −47.6 °C, is observed for EP50 (line d in Figure 1); i.e., an ethylene copolymer containing 50 wt % propylene.

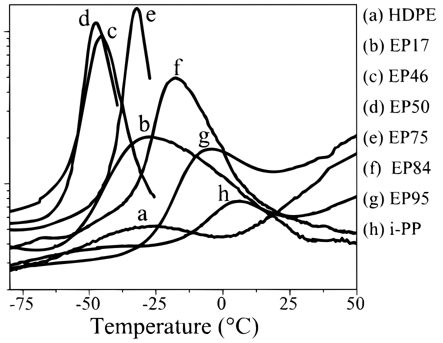


Figure 1. tan(δ) curves of HDPE and EP copolymers with different propylene content and *i*-PP. In polymer samples, code numbers behind the copolymer abbreviations denote the comonomer content in weight percent.

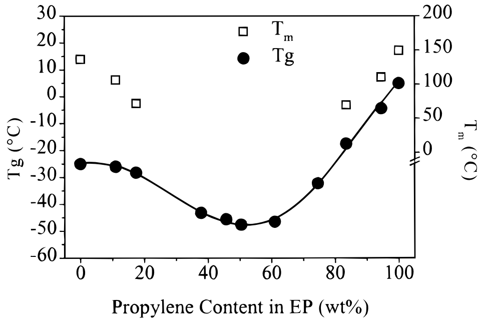


Figure 2. Glass-transition temperatures, T_g, (solid circle) and melting temperatures, T_m, (open square) of HDPE and EP copolymers with different propylene content and *i*-PP. (T_g is determined by DMA and T_m by DSC).

EP copolymers with propylene content exceeding 50 wt % show different behavior. EP75 exhibits a T_g = −32.2 °C, which is higher than that for EP50, and the maximum of tan(δ) is even higher with respect to that of EP50 as shown in line e in Figure 1. EP copolymers with propylene content exceeding 84 wt % exhibit residual crystallinity resembling homopolypropylene. These copolymers can be considered as ethylene-poor poly(propylene-*co*-ethylene), i.e., disturbed polypropylene. For a better overview, the T_g's and T_m's of all EP copolymers are plotted in Figure 2 as a function of propylene content.

Poly(ethylene-*co*-1-butene)s. Figure 3 depicts the T_g's and T_m's of EB as a function of 1-butene content. T_g is determined by means of DMA and T_m by means of DSC (see Table 2). Melting temperatures are decreasing with increasing 1-butene content from T_m = 136 °C (HDPE) to T_g = 55 °C for EB32. For EB copolymers with 1-butene contents between 48 and 72 wt %, no crystallinity is observed by either DSC or WAXS measure-

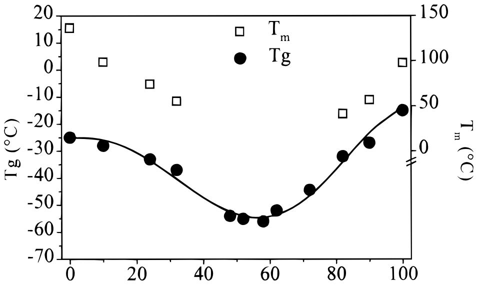


Figure 3. T_g (solid circle) and T_m (open square) of HDPE and EB copolymers with different 1-butene content and *i*-PB. (T_g is determined by DMA and T_m by DSC)

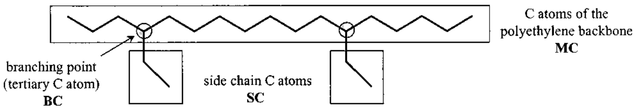
ments.[24] As expected for even higher 1-butene contents, the melting temperature increases again. For example, the melting temperature of EB82 is $T_m = 41$ °C, whereas the melting temperature of isotactic poly(1-butene) (*i*-PB) is $T_m = 98$ °C. The T_g is decreasing with increasing 1-butene content in EB from $T_g = -25$ °C for HDPE to $T_g = -56$ °C for EB58.

As shown for both EP and EB, there is a pronounced impact of comonomer content on T_g of branched polyethylene prepared by ethylene/1-olefin copolymerization. Both copolymer families are rendered amorphous when incorporating between 40 and 70 wt % 1-olefin. For both EP and EB copolymers, the minimum of the T_g is observed at a comonomer content of about 50−60 wt %.

For the ethylene copolymers with 1-hexene and 1-octene, the minimum of T_g is observed at a comonomer content of about 60−65 wt %. T_g's of the respective isotactic homopolymers are $T_g = -27.6$ °C for *i*-PH and $T_g = -52.1$ °C for *i*-PO ($T_g = 6.3$ °C for *i*-PP and $T_g = -15.2$ °C for *i*-PB). For evaluation of the influence of the degree of branching on polyethylene T_g, only ethylene-rich copolymers are examined.

Degree of Branching. From Tables 1−4, it is apparent that the same T_g can be obtained with different molecular architectures of branched polyethylenes, resulting from different stereoregularity, regioregularity, sequence distribution, and especially different lengths of the *n*-alkyl branches. The length of short chain branches can be varied by increasing the length of the *n*-alkene comonomer. Furthermore, the number of short chain branches can be adjusted by varying 1-olefin incorporation. To extract the role of short chain branching in polyethylene, ethylene-rich copolymers are examined with respect to correlations of T_g and degree of branching. It should be noted, however, that there exist different approaches to calculate the degree of branching. Brookhart et al. define "the amount of branching as the number of branches per 1000 of the total methylene (−CH_2−) groups in the polymer.... These methylene groups include those in the main chain and in the branches."[27] This definition is based upon ^{1}H NMR analysis, where the methyl groups give a signal at 0.87 ppm and the methylene and methine groups give a signal at about 1.0−1.2 ppm. On the other hand, "the degree of branching (DB) can be estimated from ^{1}H NMR integration of the methyl, methylene, and methine groups" and thus yield, for instance, a "polyethylene with 103 branches/1000 carbon atoms."[19] These definitions of the degree of branching are used because they can be easily calculated from ^{1}H NMR analysis.

Scheme 2. Microstructure of *n*-Alkyl Branched Polyethylene[a]



[a] Main chain carbons (MC) include methylene and methine groups of the backbone. Side chain carbons (SC) involve the carbon atoms of the branch.

Table 6. Calculation of Degrees of Branching

Definition	Abbr.			Fig. 4[d]
$[E]_{polym}$ (mol%)	F_E			
$[X]_{polym}$ (mol%) [a]	F_X			
Number of Main Chain Carbon[b]	MC	$MC = 2 \cdot (F_X + F_E) = 2 \cdot 100$	eq. 1	
Number of Branching Carbon	BC	$BC = F_X$	eq. 2	
Number of Side Chain Carbon	SC	$SC = (X-2) \cdot F_X$	eq. 3	
DB [c]	$\frac{BC}{1000 \cdot (MC+SC)}$	$= \frac{F_X}{200+(X-2) \cdot F_X} \cdot 1000$	eq. 4	A1
	$\frac{BC}{1000 \cdot MC}$	$= \frac{F_X}{200} \cdot 1000$	eq. 5	A2
	$\frac{BC}{1000 \cdot (MC-BC)}$	$= \frac{F_X}{200-F_X} \cdot 1000$	eq. 6	A3
	$\frac{SC}{1000 \cdot (MC+SC)}$	$= \frac{(X-2) \cdot F_X}{200+(X-2) \cdot F_X} \cdot 1000$	eq. 7	B1
	$\frac{SC}{1000 \cdot MC}$	$= \frac{(X-2) \cdot F_X}{200} \cdot 1000$	eq. 8	B2
	$\frac{SC}{1000 \cdot (MC-BC)}$	$= \frac{(X-2) \cdot F_X}{200-F_X} \cdot 1000$	eq. 9	B3
	$\frac{SC+BC}{1000 \cdot (MC+SC)}$	$= \frac{(X-1) \cdot F_X}{200+(X-2) \cdot F_X} \cdot 1000$	eq. 10	C1
DB*	$\frac{SC+BC}{1000 \cdot MC}$	$= \frac{(X-1) \cdot F_X}{200} \cdot 1000$	eq. 11	C2
	$\frac{SC+BC}{1000 \cdot (MC-BC)}$	$= \frac{(X-1) \cdot F_X}{200-F_X} \cdot 1000$	eq. 12	C3

[a] X denotes the number of C atoms in 1-olefin (e.g., $X = 3$ for propylene) with $X \geq 3$. [b] Factor two origins from methylene and methine unit per ethylene and 1-alkene in the main chain of copolymer. [c] Johnson et al.[19] [d] See Figure 4.

To elucidate the differences between these approaches, a simple model of branched polyethylenes classifying the different types of carbon atoms is presented in Scheme 2. The number of carbon atoms in the polyethylene backbone, including methylene and methine units, is denoted as MC (main chain carbons). SC (side chain carbons) covers all C atoms of the side chain, i.e., methylene and methyl groups without the methine C atoms in the backbone. The number of branching points, i.e., tertiary carbon atoms of the PE backbone, is abbreviated as BC (branching carbons). BC takes into account the defects in the polyethylene chain resulting from incorporation of a tertiary C atom. It has to be stressed that MC includes BC. The number for MC, BC, and SC can be calculated from the molar fraction of ethylene in the branched polyethylene, $[E]_{polym}$ in Table 6 and the comonomer molar fraction $[X]_{polym}$ (cf. eqs 1−3 in Table 6).

It is apparent from Scheme 2 that there exist several possibilities to define a degree of branching, e.g., considering BC or SC. Furthermore, it is possible to relate DB not only to 1000 C atoms or 1000 methylene groups but also to 1000 C atoms of the PE main chain. Most approaches ignore the number of the C atoms in the side chain (SC) and use either the ratio of BC to 1000 C atoms (MC + SC) or, alternatively, the ratio of BC to 1000 methylene groups (backbone and side chain) to calculate the degree of branching.[16,19,28] We also

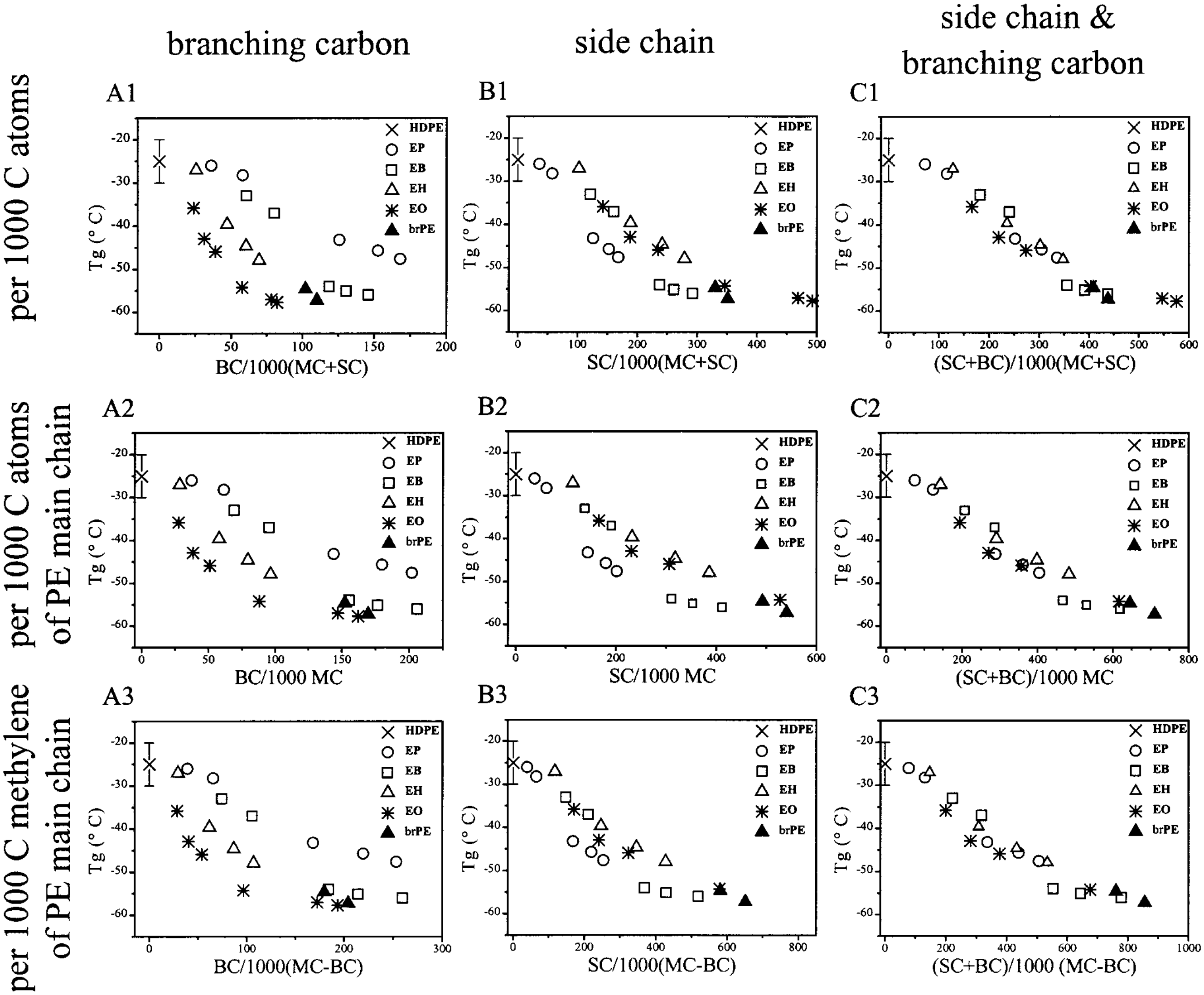


Figure 4. T_g of poly(ethylene-*co*-1-alkene) as a function of various degree of branching. (A1) BC/1000 (MC + SC), (B1) SC/1000 (MC + SC), (C1) (SC + BC)/1000 (MC + SC); (A2) BC/1000 MC, (B2) SC/1000 MC, (C2) (SC + BC)/1000 MC; (A3) BC/1000 (MC − BC), (B3) SC/1000 (MC − BC), (C3) (SC + BC)/1000 (MC − BC).

include the number of the carbon atoms in the side chain (SC). The different degrees of branching are summarized in Table 6: SC refers to 1000 MC (eq 8), SC refers to all carbon atoms (eq 7), and SC refers to methylene units of the PE backbone (eq 9); the sum of SC and BC refers to 1000 MC (eq 11), the sum of SC and BC refers to 1000 (MC + SC) (eq 10), and the sum of SC and BC refers to 1000 (MC − BC), i.e., only the methylene C atoms of the backbone (eq 12).

The degrees of branching calculated according to the different approaches illustrated in Table 6 (eq 4 DB and eq 11 DB*) are listed in Table 1 for EP, Table 2 for EB, and Table 3 for EH and EO. In Table 4 is included also brPE. brPE contains mainly *n*-alkyl branches, i.e., methyl to hexyl and longer branches.

T_g versus Degree of Branching. In Figure 4, the T_g's of all ethylene-rich copolymers including brPE are plotted versus the different degrees of branching that are defined in Table 6. In the first row, the degree of branching is related to all C atoms (MC + SC). In the second row, the degree of branching is related to the complete PE backbone (MC). In the third row, the degree of branching is related to the methylene groups of the backbone neglecting the tertiary C atoms (MC − BC). In the first column, the degree of branching takes into account only the branching points (BC). However, in the second column, the degree of branching includes the number of C atoms in the side chain (SC). In the third column, the degree of branching takes into account the side chain and even the branching points (SC + BC).

From Figure 4, it is apparent that the conventional approaches BC/1000 (MC + SC) (A1, eq 4) and BC/1000 MC (A2, eq 5) fail to afford a simple correlation. Copolymers having a similar DB of ≈60, i.e., DB(EP17) = 58, DB(EB24) = 61, DB(EH36) = 60, and DB(EO48) = 58, exhibit different T_g's such as T_g(EP17) = −28 °C, T_g(EB24) = −33 °C, T_g(EH36) = −45 °C, and T_g(EO48) = −54 °C. If the same amount of 1-olefin is incorporated in ethylene-rich copolymers (similar DB = BC/1000 (MC + SC)), 1-octene gives a lower T_g compared with that of propylene.

In contrast, better correlation is found when the number of side chain carbon is taken into account (Figure 4, B1−B3). Master curves are obtained when the number of the entire branches including the branched carbon C in the main chain (sum of BC and SC) is taken into account (Figure 4, C1-C3), especially when referred to 1000 C of the PE backbone, corresponding to DB* =

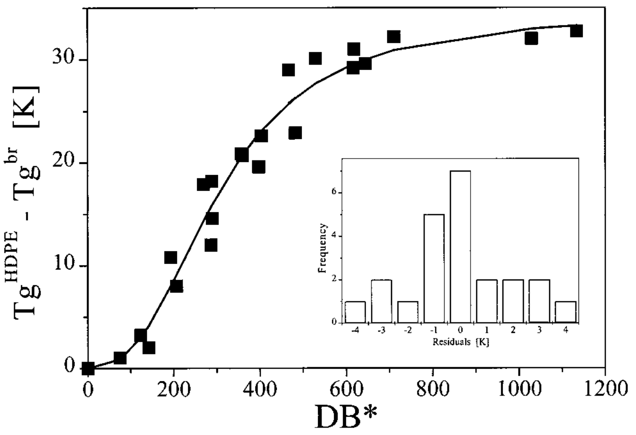


Figure 5. $T_g^{HDPE} - T_g^{br}$ as a function of DB* (eq 11) and the respective sigmoidal fit (eq 13). The inset shows a histogram of the residuals that are distributed normally.

Table 7. Fit Parameters of Sigmoidal Fit[a]

$$\left(Tg^{HDPE} - Tg^{br}\right) = \frac{a}{1 + \left(\frac{x_0}{DB^{def}}\right)^b} \qquad (13)$$

DB^{def}	Eq.	a [K]	b	x_0 [K]	R
$= \frac{(X-1) \cdot F_X}{200 + (X-2) \cdot F_X} \cdot 1000$	10	37.8	2.84	269	0.964
$DB^* = \frac{(X-1) \cdot F_X}{200} \cdot 1000$	11	34.4	2.60	306	0.965
$= \frac{(X-1) \cdot F_X}{200 - F_X} \cdot 1000$	12	34.9	2.27	345	0.966

[a] $T_g^{HDPE} = -25$ °C (T_g^{br} is T_g of branched polyethylene, DB^{def} is the respective degree of branching, and x_0 is the inflection point).

(SC + BC)/1000 MC (Figure 4 C2, eq 11). For instance, copolymers having a similar DB* of ≈380, i.e., DB*(EP46) = 360, DB*(EH36) = 398, and DB*(EO31) = 357 exhibit almost the same T_g in the range from $T_g = -45$ to -46 °C. The same T_g can be achieved by incorporating either small amounts of 1-octene or larger amounts of propylene.

For convenience, $T_g^{HDPE} - T_g^{br}$, i.e., the difference between the T_g of HDPE and T_g of branched polyethylenes under investigation, is plotted versus the degree of branching calculated according to eqs 10−12. Exemplary the data points are shown for DB* (eq 11) in Figure 5.

For 100 < DB* < 500, the difference $T_g^{HDPE} - T_g^{br}$ displays an almost linear dependence on DB*, whereas for DB* > 500, $T_g^{HDPE} - T_g^{br}$ levels off and reaches a plateau value. Because of this behavior, the data points of all branched polyethylenes under investigation are fitted to a three-parameter sigmoidal function. The function used is given by eq 13, and the resulting fitting parameters are summarized in Table 7.

$$(T_g^{HDPE} - T_g^{br}) = \frac{a}{1 + \left(\frac{x_0}{DB^{def}}\right)^b} \qquad (13)$$

The quality of the fit is given by the regression coefficient R. For all cases (eqs 10−12), R is about 0.96, indicating that eqs 10−12 are capable of describing the DB − T_g correlation correctly. x_0 corresponds to the inflection points of the curves. For $DB^{def} \gg x_0$, the T_g of branched polyethylenes reaches a minimum value of $T_g^{br} = (T_g^{HDPE} - a) = -62.8$ °C for eq 10, −59.4 °C for eq 11, and −59.9 °C for eq 12. The range of DB^{def} values is increasing in the order C1 < C2 < C3, and thus the value of x_0 is becoming larger in the same order. The inset in Figure 5 shows a histogram of the residuals that can be considered as distributed normally. This provides strong indication that a sigmoidal function can be used to describe the ($T_g^{HDPE} - T_g^{br}$) − DB correlation properly. Although the fits are of nearly the same quality, we recommend the application of eq 11 for the definition of DB* because in eq 11 the comonomer content F_x appears only once in the numerator.

T_g's of all investigated ethylene copolymers correlate with DB* in the temperature range between −30 and about −55 °C. Thus, this degree of branching DB* is a useful quantity to correlate T_g with short chain branching. By taking into account the total length of the *n*-alkyl branch with respect to the PE backbone, DB* allows one to calculate the composition of ethylene copolymers required to reach a certain T_g. The correlation can be also used to estimate the effect of terpolymer formation on the lowering of the T_g of EP or EB copolymers by incorporating 1-octene as termonomer. Further research is required to establish whether this correlation holds for branched polyethylenes containing branched side chains such as poly[ethylene-*co*-(4-methyl-1-pentene)].

Conclusions

The glass-transition temperatures of *n*-alkyl branched polyethylenes containing mainly *n*-alkyl short chain branches is dependent on the number of short chain branches as well as on the branch length given by the number of C atoms in the side chain including the tertiary C atom of the branch point in the main chain. The conventional approach refers the number of branching points (BC) to 1000 C atoms of the polyethylene (MC + SC), thus defining DB as equal to BC/1000 (MC + SC). However, no correlation between the DB and T_g of *n*-alkyl branched polyethylenes results. It is more preferable to take into account both the number and length of the branches with respect to the C atoms of the PE backbone, thus using DB* defined as (BC + SC)/1000 MC. This correlation gives a clear explanation of why branched polyethylene, prepared with Pd catalysts and containing large amounts of hexyl side chains, exhibits very low T_g's compared to those of metallocene-catalyzed ethylene/propylene copolymers. From Figure 4, it is apparent that a low T_g corresponds not only to a high number of BC but also a high number of SC. A high number of SC is found for polyethylene with very high content of hexyl and longer branches. Similar low T_g's can be reached when ethylene is copolymerized with 1-octene. Furthermore, the T_g of EP can be lowered by means of terpolymerization of ethylene/propylene with 1-octene. Limitation of the correlation is the minimum T_g of about −60 °C that can be reached for a certain branch type.

Acknowledgment. The authors thank the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (Project #03D0055 1) for financial support and BASF AG, Ludwigshafen. Furthermore, the authors thank Prof. H. A. Schneider and PD Dr. Dr. Chr. Friedrich for intense discussion and helpful annotations.

References and Notes

(1) Brintzinger, H.-H.; Mülhaupt, R.; Fischer, D.; Rieger, B.; Waymouth, R. *Angew. Chem.* **1995**, *107*, 1255.

(2) Bensason, S.; Minick, J.; Moet, A.; Chum, S. P.; Hiltner, A.; Baer, E. *J. Polym. Sci., Polym. Phys.* **1996**, *34*, 1301.

(3) Minick, J.; Moet, A.; Hiltner, A.; Baer, E.; Chum, S. P. *J. Appl. Polym. Sci.* **1995**, *58*, 1371.

(4) Bensason, S.; Stepanov, E. V.; Chum, S.; Hiltner, A.; Baer, E. *Macromolecules* **1997**, *30*, 2436.

(5) Kravchenko, R.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 1.

(6) Jüngling, S.; Koltzenburg, S.; Mülhaupt, R. *J. Polym. Sci., Part A* **1997**, *35*, 1.

(7) Suhm, J.; Schneider, M. J.; Mülhaupt, R. *J. Mol. Catal., Part A* **1998**, *128*, 215.

(8) Rossi, A.; Zhang, J.; Odian, G. *Macromolecules* **1996**, *29*, 2332.

(9) Quijada, R.; Dupont, J.; Miranda, M. S. L.; Scripioni, R. B.; Galland, G. B. *Macromol. Chem. Phys.* **1995**, *196*, 3391.

(10) Schneider, M. J.; Suhm, J.; Mülhaupt, R.; Prosenc, M.-H.; Brintzinger, H.-H. *Macromolecules* **1997**, *30*, 3164.

(11) Schneider, M. J.; Mülhaupt, R. *J. Mol. Catal., Part A* **1995**, *101*, 11.

(12) Suhm, J.; Schneider, M. J.; Mülhaupt, R. *J. Polym. Sci., Part A* **1997**, *35*, 735.

(13) Suhm, J.; Heinemann, J.; Thomann, Y.; Thomann, R.; Maier, R.-D.; Schleis, T.; Okuda, J.; Kressler, J.; Mülhaupt, R. *J. Mater. Chem.* **1998**, *8*, 553.

(14) Gianotti, G.; Dall'Asta, G.; Valvassori, A.; Zamboni, V. *Makromol. Chem.* **1971**, *149*, 117.

(15) Krigas, T. M.; Carella, J. M.; Struglinsky, M. J.; Crist, B.; Graessley, W. W.; Schilling, F. C. *J. Polym. Sci., Part B* **1985**, *23*, 509.

(16) Gerum, W.; Höhne, G. W. H.; Wilke, W.; Arnold, M.; Wegner, T. *Macromol. Chem. Phys.* **1996**, *197*, 1691.

(17) Mäder, D.; Thomann, Y.; Suhm, J.; Mülhaupt, R. *J. Appl. Polym. Sci.* **1999**, *74*, 838.

(18) Möhring, V.; Fink, G. *Angew. Chem.* **1985**, *97*, 982.

(19) Johnson, L. K.; Kilian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.

(20) Heinemann, J.; Mülhaupt, R.; Brinkmann, P.; Luinstra, G. *Macromol. Chem. Phys.* **1999**, *200*, 384.

(21) Axelson, D. E.; Levi, G. C.; Mandelkern, L. *Macromolecules* **1979**, *12*, 41.

(22) Mäder, D.; Bruch, M.; Maier, R.-D.; Stricker, F.; Mülhaupt, R. *Macromolecules* **1999**, *32*, 1252.

(23) Schneider, H. A. In *Polyolefin Handbook*, 2nd ed., in press.

(24) Thomann, Y.; Suhm, J.; Thomann, R.; Bar, G.; Maier, R.-D.; Mülhaupt, R. *Macromolecules* **1998**, *31*, 5441.

(25) Heinemann, J.; Walter, P.; Mäder, D.; Mülhaupt, R. In *Metallorganic Catalysts for Synthesis and Polymerization*, 1st ed.; Kaminsky, W. Ed.; Springer: Berlin, 1999.

(26) Walter, P.; Mäder, D.; Reichert, P.; Mülhaupt, R. *J. Macromol. Sci. Pure Appl. Chem.*, in press.

(27) WO 96/23010, M. Brookhart et al. **1996**, 97.

(28) Uozomi, T.; Soga, K. *Macromol. Chem. Phys.* **1992**, *193*, 823.

MA991096O