Macromolecules **1998,** *31,* 3783−3789

ansa-Zirconocene-Catalyzed Solution Polymerization of Propene: Influence of Polymerization Conditions on the Unsaturated Chain-End Groups

Andrew Carvill, Lucia Zetta, Giulio Zannoni, and Maria Carmela Sacchi*

Istituto di Chimica delle Macromolecole del C.N.R., Via E. Bassini 15, 20133 Milano, Italy

Received January 6, 1998; Revised Manuscript Received March 27, 1998

ABSTRACT: Two series of solution polymerizations of propene were conducted: (i) using three different methylaluminoxane (MAO)-activated zirconocenes, *rac*-Et(Ind)$_2$ZrCl$_2$ (EI), *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$ (MI), and *rac*-Me$_2$Si(Benz-[e]-Ind)$_2$ZrCl$_2$ (MBI), at the same temperature (30 °C) and varying propene pressure from 0.15 to 1.1 bar and (ii) using *rac*-Me$_2$Si(Benz-[e]-Ind)$_2$ZrCl$_2$ (MBI) at the propene partial pressure 1.1 bar and at a range of temperatures from 30 to 100 °C (Ind = Indenyl). ^{1}H and ^{13}C NMR investigation of the unsaturated chain end groups in these samples was performed, with particular attention being paid to (i) a detailed re-examination of the NMR assignments reported in the literature, (ii) the distinction between unsaturated species formed during the polymerization reactions and those formed afterward due to thermal treatment (i.e. during the NMR experiments), (iii) determination of the dependence of the quantities of different types of terminals on the polymerization conditions (temperature and monomer partial pressure). It was shown that four unsaturated chain end groups are formed during polymerization, that is, vinylidene, 2-butenyl, allyl, and the previously unidentified 4-butenyl terminals. In the oligomeric fraction of samples, no further types of unsaturated terminals were observed. Two further types of unsaturated groups observed, isobutenyl and the unidentified species X, were not formed during polymerization but, at least prevalently, afterward during the high-temperature NMR experiments. A previously unidentified regiomisinsertion, lateral *n*-butyl, is also described.

Introduction

In a recent paper we have described an investigation on the hydrogen effect in Ziegler−Natta-catalyzed polymerizations of olefins. Our aim was to understand the reasons for the additional effect of an increase in catalyst activity which is observed in many cases to accompany the well-known effect of molecular weight reduction.[1] The starting point of this research was to test the hypothesis which has the greatest following, that is, that occasional secondary insertions give rise to sterically congested metal polymeryls, which are either dormant or slow to propagate, and that these sites are released by chain transfer to hydrogen.[2] Occasional secondary insertions would therefore be the origin of the hydrogen activation effect. In propene polymerization, *n*-butyl end groups resulting from chain transfer to hydrogen following secondary insertions are considered diagnostic of this mechanism.[2a,c,3] In our investigation we have tried to find a relationship between the number of *n*-butyl groups appearing and the degree of activation produced by hydrogen with a variety of isospecific zirconocene catalysts. The conclusion, based on a number of different ways of correlating variations of regioirregularities/end groups to the corresponding hydrogen activation effects, was that the reactivation of dormant sites following a 2,1 insertion can only be one of the causes of the hydrogen activation effect. In one case this hypothesis did not seem to explain the observed activation by hydrogen at all.[1]

Therefore, we are currently exploring alternative additional activation mechanisms. We believe that some kinds of unsaturated chain-end groups, which act as polymerization inhibitors and themselves are in turn inhibited by hydrogen, may also be responsible for the observed activation.[2h] Therefore, at this point an in-depth knowledge of all the unsaturated species present in the polymerization system has become important. The steps in the present investigation have been (i) a detailed re-examination of the NMR assignments of unsaturated chain-end groups reported in the literature, (ii) the distinction between unsaturated species formed during the polymerization reactions (and therefore of possible relevance to the activation mechanism) and those formed afterward due to thermal treatment (i.e. during the NMR experiments), and (iii) determination of the dependence of the quantities of different types of terminals on the polymerization conditions (monomer partial pressure and temperature) and the identification of some previously unreported terminals.

Results and Discussion

Four unsaturated chain-end groups have been so far identified in propene homopolymers.[2a,c,3a,d,4] Vinylidene terminals derive from transfer of a β-hydrogen of the growing chain to monomer or to metal after regular (1,2) monomer insertion. Isobutenyl terminals are proposed to derive from vinylidene isomerization. 2-Butenyl terminals derive from chain transfer to monomer or to metal after secondary (2,1) monomer insertion. Allyl terminals derive from β-methyl transfer to metal after primary (1,2) monomer insertion (Scheme 1).

Re-examination of the NMR Assignments of the Unsaturated Chain-End Groups. A re-examination of the assignments of the unsaturated chain-end groups which we adopted in the previous paper[1] has been made necessary by two problems which arise from a careful analysis of the olefin region of the proton NMR spectra of different samples and which could not then be accounted for. The first problem regards the fact that in some cases we observed the presence of a doublet (K) at 4.78 ppm (Figure 1a and b) which has not been reported in the literature on propene homopolymers and

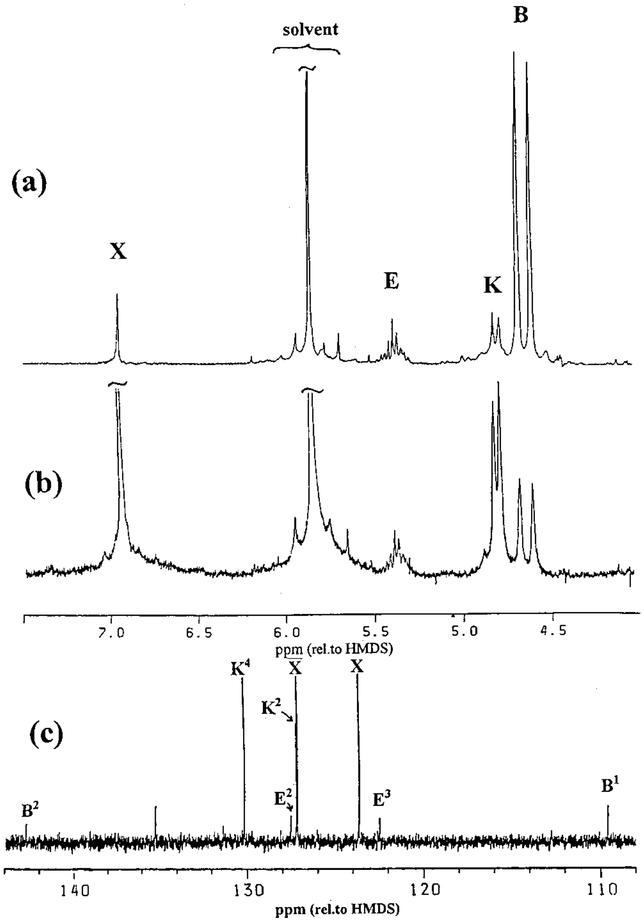
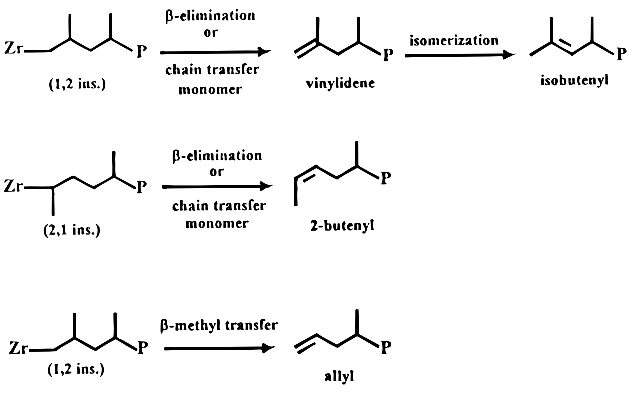


Figure 1. ^{1}H NMR spectra (recorded in 1,1,2,2-tetrachloroethane-d_2 at 103 °C) of the olefinic region of polypropene prepared using *rac*-Et(IndH$_4$)$_2$ZrCl$_2$/MAO: (a) fresh sample, recorded over 12 h; (b) same sample, recorded after heating at 103 °C for a further 48 h. (c) ^{13}C NMR spectrum (olefinic region) of the same sample in part b recorded after spectrum b.

Scheme 1. Unsaturated Chain Terminal Groups in Polypropene



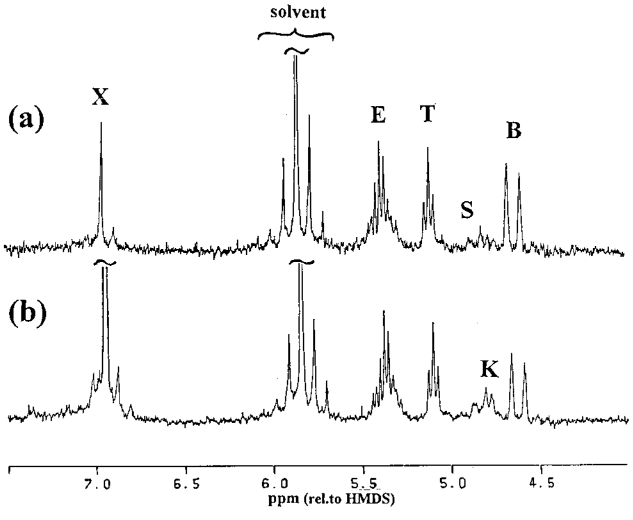


Figure 2. ^{1}H NMR spectra (recorded in 1,1,2,2-tetrachloroethane-d_2 at 103 °C) of the olefinic region of polypropene prepared using *rac*-Me$_2$Si(Benz[*e*]Ind)$_2$ZrCl$_2$/MAO (run 10a): (a) fresh sample recorded over 12 h; (b) same sample recorded after heating at 103 °C for a further 48 h.

whose presence was difficult to rationalize. Indeed not only did this doublet appear in the spectra of some polymers and not in those of others but it also appeared in variable amounts in different samples of the same polymer. A similar doublet has been assigned to the olefinic proton of the pendant isobutenyl groups of an ethene/5,7-dimethylocta-1,6-diene copolymer.[5] The second problem regards the triplet (T) centered at 5.10 ppm (Figure 2) which is observed to form in the presence of some of the catalysts used. This triplet was assigned to the isobutenyl end group which is suggested to derive from vinylidene chain-end group isomerization.[3d,4d] However, comparison among the spectra of a wide variety of samples prepared with different catalysts has shown (i) that the triplet intensity is independent of the intensity of the signals due to the vinylidene group from which it should derive and (ii) that the triplet is present only when the multiplet (E) centered at 5.37 ppm and assigned to 2-butenyl end groups is also present. The ^{13}C NMR spectrum of the isobutenyl end group has already been assigned unambiguously on the basis of a DEPT experiment.[4e]

To try to solve these two contradictions, we have analyzed the proton NMR spectra of two polymers, each of which contained only one of the signals K and T, and compared them with the corresponding ^{13}C NMR spectra. Figure 1a shows the proton NMR spectrum of a sample in which the signal T, previously assigned to the isobutenyl end group, is completely absent while the doublet K is present in a ratio of about 1 to 4 with respect to the signals B assigned to the vinylidene end group. This sample was prepared using the catalyst *rac*-Et(IndH$_4$)$_2$ZrCl$_2$/MAO, which has previously been observed to give low-molecular-weight polymers with vinylidene as the principal unsaturated terminal group.[1] Figure 1b shows the spectrum of the same sample after 48 h of heating at 103 °C. It is apparent that, while the triplet T is still completely absent, the unknown doublet K is greatly enhanced and its intensity is now about twice the intensity of the diminished vinylidene signal. Figure 1c shows the olefinic region of the ^{13}C NMR spectrum, recorded after spectrum b, on the same sample. In this spectrum, besides the signals at 142.88 and 109.32 ppm assigned to the vinilydene end group (B) and the signals at 127.50 and 122.39 ppm assigned to the 2-butenyl end group (E), two more intense signals are observed at 130.16 and 127.11 ppm, that is, exactly those which were previously assigned to the isobutenyl end group.[4e] These results clearly show that the doublet K instead of the triplet T in the proton spectrum has to be assigned to the isobutenyl end group (in fact, in spectrum c, the process of isomerization of B to K has progressed further than in spectrum b). The two remaining signals which appear in Figure 1c at 127.10 and 123.54 ppm (marked X and corresponding to a signal at 6.91 ppm in the proton spectrum) appear to be due to a degradation product rather than to any terminal group, and are discussed further below.

Figure 2a shows the proton NMR spectrum of a sample (prepared using *rac*-$Me_2Si(Benz\text{-}[e]\text{-}Ind)_2ZrCl_2$/MAO) in which the doublet K assigned to isobutenyl terminals is almost completely absent while the now unknown triplet T is present with about the same intensity as the multiplet due to the 2-butenyl end group E. This sample was also heated at 103 °C for 48 h. Figure 2b shows the spectrum of the sample after this treatment. In this case, besides a partial isomerization of vinylidene B to isobutenyl K, and a large increase in the amount of the decomposition product X, no further evolution of the system is observed, the ratio of E to T being the same as that prior to the treatment. To identify the structure corresponding to the triplet, conventional ^{13}C and ^{13}C DEPT-NMR spectra were recorded (Figure 3a and b, respectively) of samples of the same polymer. The DEPT analysis re-confirms the assignments of the vinylidene, isobutenyl, and 2-butenyl end groups. Besides the signals due to these groups and the signals X mentioned above, two pairs of very close signals at 125.47 and 125.55 ppm and 135.25 and 135.45 ppm, respectively, were observed, with intensities which corresponded to the intensity of the triplet T in the ^1H spectrum. In the DEPT experiment the higher field of these pairs was not phase-inverted (indicating that the carbons were bonded to single protons) while the second pair was missing (quaternary carbons). On the basis of these results and of the consideration that this species is observed only when the 2-butenyl end group is also formed, two possible structures, T and T′, could be suggested (Chart 1). Either of these could be a mixture of *E* and *Z* structures and so account for the presence of two close pairs. For known olefins with structures similar to T and T′ (such as 4-methyl-3-heptene) it has been shown that the differences between the carbon chemical shifts of the carbons of the double bond for the *E* and *Z* structures are less than 1.0 ppm.[6] However the ^1H NMR spectra (Figure 2) permit us to rule out structure T′ on the basis that the single olefinic proton should give a doublet with $J(CH-CH)$ in the range 4−8 Hz, while structure T explains the observed triplet with $J(CH-CH_2) = 7$ Hz. The analysis of the aliphatic region of the ^{13}C spectrum confirms the assignment of structure T to the terminal, giving rise to the triplet at 5.10 ppm in the proton spectrum. Signals appear at 11.82−11.85 ppm (primary carbon by DEPT) and at 21.26 ppm (secondary carbon) which correspond well with the adjusted chemical shifts published for C1 and C2 of the model compound 2-methyl-2-hexene.[6] In fact the chemical shift of C1 in structure T′ would be expected to be the same as that of the *n*-butyl terminal, at 12.06 ppm.

Distinction between the Unsaturated Species Formed during Polymerization and Those Due to Subsequent Treatment of the Polymer. At this point it was fundamental to distinguish unsaturated chain-end groups formed during polymerization, due to termination reactions, or metal-catalyzed isomerization (and so possibly involved in the hydrogen activation mechanism) from those which are formed when the polymer samples are heated, for example during the NMR experiments. We have shown that vinilydene end groups evolve, when the sample is heated at 103 °C, to isobutenyl end groups, whose amount increases as long as the heating is prolonged. However, in principle, one cannot exclude that variable amounts of isobutenyls could be already formed during polymerization. To clarify this point, a polymerization mixture containing the catalyst *rac*-$Et(IndH_4)_2ZrCl_2$ (which commonly showed variable amounts of isobutenyls in NMR spectra measured at 103 °C) was treated so as to be freed of catalyst traces before precipitation of the polymer. In the proton spectrum the doublet K was not observed, while very intense signals of vinilydenes were present. The doublet due to isobutenyl did not appear even when the same sample was heated at 103 °C for 48 h. These experiments indicated that, at least in the case of this catalyst, isobutenyls were not formed during polymerization but could be due to acid-catalyzed vinilydene isomerization promoted by residual catalyst during the heating of the polymer.[4e] With regard to the signals marked X in the spectra, it was found that these also only appear upon heating of the samples during the NMR experiments, eventually becoming greater than the sum of all other terminals. Close examination of spectra of a polymer sample (run 10a) recorded before and after a period of 100 h of heating at 103 °C showed that the signals X, unlike the isobutenyls K, do not appear at the expense of any of the other terminals or enchained regioirregularities. We have therefore assigned them to an as yet unidentified product, which is formed upon heating of the polymer in the NMR solvent and is unrelated to any of the chain terminals or unsaturations occurring during the polymerization reaction.

On the other hand the multiplet E assigned to 2-butenyl was always present in the same amount for a given sample, independently of whether the sample had been freed from traces of catalyst, and no evolution of this group occurs during the NMR experiment, as can be seen in the spectra of Figure 1a and b and Figure 2a and b. The same is true for the triplet T assigned to the 4-butenyl end group, which does not derive, for example, from 2-butenyl isomerization during the NMR experiment but which is present from the outset in constant proportion to the other end groups.

Dependence of Chain-End Group Trends on Polymerization Conditions. Polymerizations were conducted using three different zirconocenes, *rac*-$Et(Ind)_2ZrCl_2$ (EI), *rac*-$Me_2Si(Ind)_2ZrCl_2$ (MI), and *rac*-$Me_2Si(Benz\text{-}[e]\text{-}Ind)_2ZrCl_2$ (MBI), at the same temperature (30 °C), varying propene pressure from 0.15 to 1.1 bar. A second series of polymerizations were conducted using $Me_2Si(Benz\text{-}[e]\text{-}Ind)_2ZrCl_2$ at the propene partial pressure 1.1 bar and at a range of temperatures from 30 to 100 °C.[7] Table 1 shows the numbers (per 10 000 monomer insertions) of all end groups and enchained regioirregularities of these polypropenes, based on analysis of the integrated signals of the ^1H and ^{13}C NMR spectra. Table 2 reports the ^1H and ^{13}C NMR chemical shifts assigned under our conditions to all the chain-end groups and regioirregularities observed.

We will first discuss the trends in the numbers of unsaturated chain-end groups. The number of vinylidenes (column I) increased in general, with decreasing monomer pressure and increasing temperature. The number of 2-butenyls (column II) also increased with decreasing monomer pressure (at a given temperature, the lowest numbers were observed at the highest pressure used, 1.1 bar, runs 4, 6, and 8) and increasing temperature (at a given pressure, the lowest number was observed at the lowest temperature used, 30 °C,

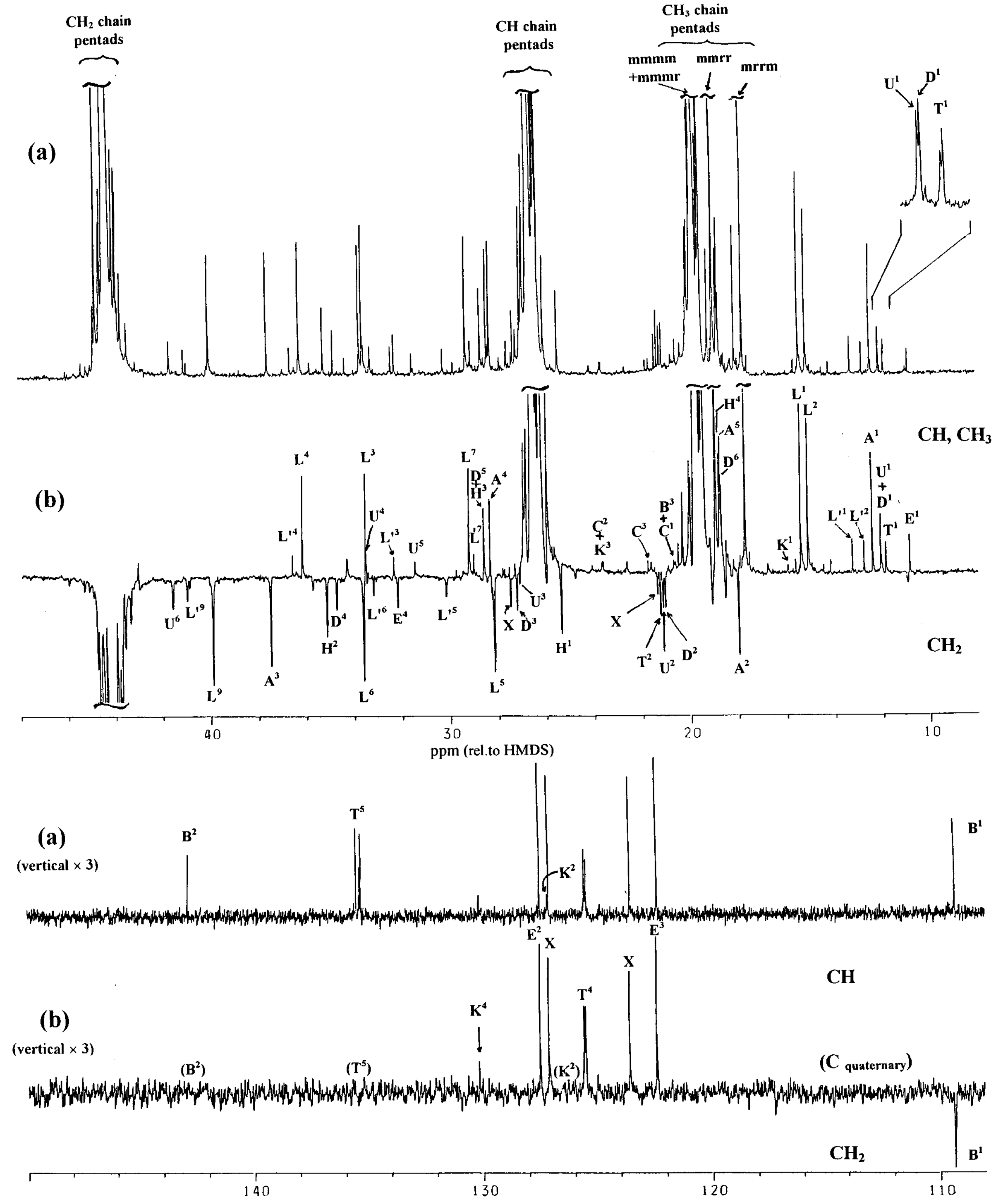
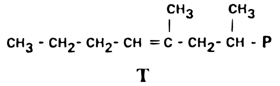


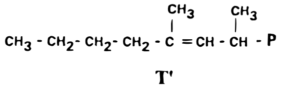
Figure 3. (a) Normal ^{13}C NMR spectrum and (b) ^{13}C DEPT NMR spectrum (recorded in 1,1,2,2-tetrachloroethane-d_2 at 103 °C, in each case over 36 h) of polypropene prepared using *rac*-Me$_2$Si(Benz[*e*]Ind)$_2$ZrCl$_2$/MAO (run 10a). Signal labeling as in Chart 2.

run 8). A notable exception to this trend was run 1, in which a propene partial pressure as low as 0.15 bar was used. In such starved catalyst conditions (as evidenced also by the sharp drop in tacticity of the polymer formed) the formation of 2-butenyl was nearly suppressed due to the competitive 2,1 to 1,3 regioerror transformation. 4-Butenyls (column III) were strongly dependent on the 2-butenyl trend and were present only when 2-butenyls were also present (in runs 1 and 6, where only small

Chart 1


$CH_3-CH_2-CH_2-CH=\overset{CH_3}{\overset{|}{C}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-P$

T


$CH_3-CH_2-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-\overset{CH_3}{\overset{|}{CH}}-P$

T'

Table 1. Polymerization Conditions and Polymer Microstructural Analysis by ^{13}C and ^{1}H NMR

polymerization conditions[b]					terminal groups and enchained regioirregularities, per 10 000 momomer insertions[a]											tacticity
					unsaturated terminals				saturated terminals			regioirregularities				
run	catalyst[c]	$p(C_3H_6)$[d]/ bar	solv.[e]	temp/ °C	I vinylidene[f]	II 2-butenyl	III 4-butenyl	IV allyl	V *n*-propyl	VI isobutyl	VII *n*-butyl	VIII int.[g] *n*-butyl	IX 2,1 erythro	X 2,1 threo	XI 1,3	XII % mmmm[h]
1	EI	0.15	tol	30	33	3	n.d.	n.d.	36	28	trace	16	14	4	36	0.77
2	EI	0.4	tol	30	22	11	6	n.d.	28	n.d.	n.d.	trace	29	26	15	0.87
3	EI	0.8	tol	30	15	13	6	n.d.	24	n.d.	n.d.	n.d.	36	22	7	0.89
4	EI	1.1	tol	30	15	7	4	n.d.	25	trace	n.d.	n.d.	48	21	5	0.88
5	MI	0.4	tol	30	9	7	3	n.d.	16	trace	n.d.	trace	27	14	3	0.93
6	MI	1.1	tol	30	9	4	trace	n.d.	15	trace	n.d.	trace	35	18	3	0.93
7	MBI	0.4	tol	30	8	14	6	n.d.	22	trace	n.d.	n.d.	63	11	3	0.93
8	MBI	1.1	tol	30	6	10	2	n.d.	22	n.d.	n.d.	trace	79	12	trace	0.92
9	MBI	1.1	tol	60	36	15	21	2	87	10	9	18	52	12	12	0.85
10a	MBI	1.1	DCB	60	9	17	19	trace	48	4	18	14	86	13	18	0.88
10b[i]	MBI	1.1	DCB	60	38	61	30	6	180	20	50	13	80	15	44	0.69
11	MBI	1.1	DCB	100	94	13	19	15	94	24	15	60	15	n.d.	85	0.64

[a] n.d, not detected; trace, signals close to the limit of detection, ca. 2/10 000 insertions. [b] Polymerizations conducted as described in ref 1, typically at the catalyst concentration 20 μmol·dm^{-3} of methylaluminoxane in the Al/Zr ratio 3000:1. [c] Catalysts: EI, *rac*-$Et(Ind)_2ZrCl_2$; MI, *rac*-$Me_2Si(Ind)_2ZrCl_2$; MBI, *rac*-Me_2Si(Benz-[*e*]-Ind)$_2ZrCl_2$. [d] Partial pressure of propene. [e] Solvents: tol, toluene; DCB, *o*-dichlorobenzene. [f] Sum of vinylidene and isobutenyl derived from vinylidene during accumulation of the NMR spectrum. [g] Internal *n*-butyl groups, that is, those replacing main-chain methyls. [h] Calculated according to least-squares fit of the observed integrals for the four principal methyl pentads to an enantiomorphic site control model (ref 12). [i] 10b was a minor oligomeric fraction of run 10; see Experimental Section.

Table 2. ^{13}C and ^{1}H NMR Signals of Chain Terminal Group Regioirregularities in Polypropenes[a]

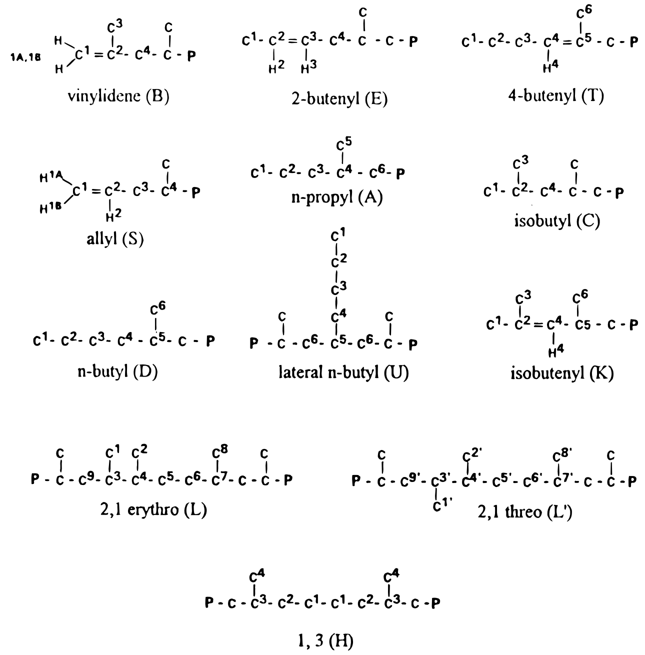
groups[d]		^{13}C NMR chemical shifts[b] (ppm relative to HMDS[c])									^{1}H NMR chemical shifts[b] (olefinic region, ppm relative to HMDS[c])
		C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	
vinylidene	(B)	109.32	142.88	20.53	h						4.59 (H^{1A}, singlet); 4.66 (H^{1B}, singlet)
2-butenyl	(E)	10.87	122.40	127.51	32.24						5.38 (H^2 and H^3, complex multiplet)
4-butenyl	(T)	11.83/11.85	21.26	h	125.47/ 125.55	135.25/ 135.45					5.11 (triplet of multiplets, H^4, $J = 7.0$ Hz)
allyl	(S)	113.48	135.57	39.23	h						4.88 (H^{1A}, broad singlet); 4.94 (H^{1B} doublet, $J = 6.2$ Hz); 5.72 (H^2, complex multiplet)
n-propyl	(A)	12.42	18.02	37.46	28.28	18.70	h				
isobutyl	(C)	20.44	23.61	21.74	h						
n-butyl	(D)	12.05	21.05	27.22	34.71	28.53	18.73				
int. *n*-butyl	(U)	12.06	21.15	27.11	31.45	33.46	41.58				
int. *n*-butyl	(model)[e]	12.06	21.16	27.11	31.44	33.46	41.57				
2,1 erythro	(L)	15.34	15.07	33.47	36.10	28.13	33.60	29.14	h	39.85	
2,1 threo	(L′)	13.21	12.70	32.30	36.55	30.14	33.16	28.96	h	40.95	
1,3	(H)	25.39	35.16	28.58	18.76						
isobutenyl	(K)	15.94	127.17	23.67	130.16	28.48	h				4.79 (H^4, doublet of multiplets, $J = 9.4$ Hz, 1.5 Hz)
	(X)[f]		21.37 (CH_2); 27.50 (CH_2); 123.55 (CH); 127.10 (CH)								6.91 (singlet)

[a] 0.25 g polymer samples in 2 cm^3 of 1,1,2,2-tetrachloroethene-d_2, recorded at 103 °C. [b] Previous literature on NMR assignments: refs 3a and 13 (^{13}C aliphatic region); refs 2a and 4 (^{13}C olefinic region); refs 3d and 4a, c, and d (^{1}H olefinic region). [c] ppm (relative to hexamethyldisiloxane, HMDS) approximately equal to δ(TMS) − 2.0 ppm for ^{13}C and to δ(TMS) − 0.06 ppm for ^{1}H. [d] Groups and atom numbering as shown in Scheme 3, h implies signal not identified or hidden by other groups. [e] Signals for enchained 1-hexene in 97:3 propene/1-hexene copolymer. [f] Unidentified group formed during accumulation of NMR spectrum at 103 °C; carbon types by DEPT NMR.

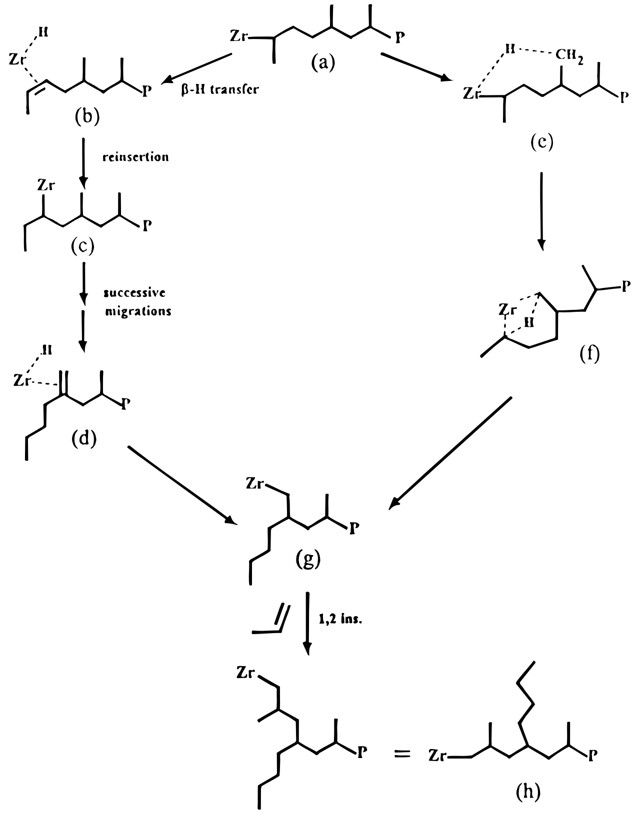
amounts of 2-butenyl were detectable, 4-butenyls were not observed at all). It was previously observed[1] that the introduction of molecular hydrogen into the polymerization reaction mixture suppresses the triplet T due to 4-butenyl, to the same extent as it suppresses the formation of 2-butenyl. 4-Butenyl formation was also favored by low monomer concentration and high temperature. It is noteworthy that increasing the temperature produced noticeably higher enhancement in 4-butenyl than in 2-butenyl formation. A temperature increase from 30 to 60 °C (runs 8−9) produced a 1.5-fold increase in the number of 2-butenyls but a 10-fold increase in 4-butenyls. Allyl end groups (column IV) were formed, as expected, only at the higher temperatures.[4b−d] The dependence of 2,1 and 1,3 enchained misinsertions on temperature and monomer concentration was as previously reported.[3c] With regard to saturated chain-end groups, at 30 °C and within the pressure range 0.4−1.1 bar, the only "left" end groups observed were *n*-propyl (column V). This indicates that, under these conditions, only chain transfer to monomer or to metal occurs. In starved conditions at 30 °C (run 1) a notable number of isobutyl groups (column VI) were detected,[3c] consisting of both the "right" and "left" end groups, likely deriving from chain transfer to $Al(CH_3)_3$ (coordinated to MAO) after a regular 1,2 insertion and subsequent regular initiation into the resulting metal−methyl bond, respectively. In the samples prepared at higher temperatures *n*-butyl end groups (column VII) were also formed, which are usually observed on chain transfer in the presence of molecular hydrogen but which in this case may derive from chain transfer to $Al(CH_3)_3$ after a 2,1 momomer insertion. In these cases isobutyl groups also appear, as would be expected, since there should be an isobutyl right end group produced by reinitiation of chain growth from the Zr−methyl bond formed with each *n*-butyl terminal. However, in run 10 (a and b) the isobutyls observed were significantly fewer than the *n*-butyls, suggesting that some other mechanism may be involved in the formation of these terminals.

Under starved catalyst conditions with $Et(Ind)_2ZrCl_2$ at 30 °C (run 1) and with Me_2Si(Benz-[e]-Ind)$_2ZrCl_2$ at higher temperatures (runs 9−11) we observed six signals due to carbons of a further saturated structure, which on the basis of comparison with the spectrum of a random 3% 1-hexene/97% propene copolymer[9] were

Chart 2. Group Labeling and Atom Numbering Used in the Figures and Table 2 with, for Simplicity, Only the Assigned (Olefinic) Protons Shown



Scheme 2. Possible Mechanisms for the Formation of the Lateral *n*-Butyl Group in Propene Homopolymerization



assigned unambiguously to lateral *n*-butyls, replacing isolated main-chain methyls (Table 2, Chart 2, group U). This group may result from migration of the Zr−C bond formed following a 2,1 monomer insertion (Scheme 2a) along the chain through a sequence of repeated β-hydride transfer (b), olefin rotation, and reinsertion (c) events, leading eventually to the metal polymeryl (g). Alternatively, the internal *n*-butyls may result from intramolecular activation of a C−H bond of the first methyl of the chain (Scheme 2e), resulting in Zr−alkyl isomerization (f) to give the same metal polymeryl (g). In either case, further primary monomer insertions would lead to the observed lateral *n*-butyl group (h).[4b,10,11]

In general the polymers were collected by adding the reaction mixture to acidified ethanol. For run 10 the small oligomeric fraction which remained in solution in the DCB/ethanol mixture was recovered as described in the Experimental Section. The ^{1}H and ^{13}C NMR analysis shows that the unsaturated chain-end groups of this fraction were qualitatively the same as those in the main fraction but in greater numbers due to the low molecular weight. The same trend was observed on the basis of the ^{1}H NMR spectra, for oligomeric fractions collected in the same way for several other polymers. This suggested that this more soluble, lower molecular weight portion of the polymer did not represent oligomers formed by alternative chain termination mechanisms.

Conclusions

Detailed NMR investigation of the unsaturated chain-end groups in polypropenes prepared using MAO-activated *ansa*-zirconocenes in solution polymerization has been performed, with particular attention being paid to distinguish the species formed during the polymerization and to evidence the polymerization conditions which favor their formation. The following points were shown:

(i) Four unsaturated chain-end groups are formed during polymerization: vinylidene, 2-butenyl, 4-butenyl, and allyl terminals. In oligomeric fractions, no further terminal types were observed.

(ii) The numbers of these four terminals depended on the polymerization conditions. Allyls were formed only at relatively high polymerization temperatures. The formation of vinylidenes, 2-butenyls, and 4-butenyls was in general favored by low pressure and high temperature. It appears that the formation of 4-butenyl is linked to that of 2-butenyl during the polymerization, although 4-butenyl was not produced by isomerization of 2-butenyl upon thermal treatment of the already formed polymer.

(iii) The other two unsaturated species detected, isobutenyls and the unidentified species X, were formed, at least prevalently, during the high-temperature NMR experiments.

Therefore, if unsaturated groups formed during the polymerization are acting as inhibitors and the hydrogen activation effect is due in part to release of this inhibition, the unsaturated groups involved should be found among the above-mentioned four species.

This investigation has also shown that (i) at relatively high temperatures *n*-butyl terminals are formed even in the absence of hydrogen and (ii) both higher temperatures and starved conditions favor the formation of the lateral *n*-butyl group, which has not been observed previously. We are currently investigating further the mechanism for the production of this group, for which intermediates could be involved in the blocking of catalytic sites and so also be implicated in the hydrogen activation effect.

Experimental Section

Catalyst Preparation and Polymerizations. All operations were carried out under a dry nitrogen atmosphere by using drybox and standard vacuum Schlenk techniques. Nitrogen, hydrogen, and propene were purified by passage through columns of BASF RS-11 (Fluka) and Linde 4 Å molecular sieves. Methylaluminoxane (MAO, 30% w/w toluene solution, Schering) was used after removing all volatiles and drying the resulting white powder in a vacuum (12 h, room temperature, 0.1 mbar). Toluene was dried by distillation from molten sodium under purified nitrogen. Zirconocene catalysts were used as obtained from commercial sources (Witco) or as kindly supplied by Prof. H. H. Brintzinger. The typical polymerization procedure was the same as described in ref 1, nitrogen being used to bring the total pressure in the reaction flask to 1.1 bar, in the reactions with propene partial pressure of less than 1.1 bar. In general, reactions were stopped at 60 min by addition of a small amount of ethanol, and polymers were precipitated by addition of the whole reaction mixture (100 cm^3) to ethanol (600 cm^3) to which concentrated hydrochloric acid (5 cm^3) had been added. The precipitated polymers were washed with ethanol and dried under vacuum at 60 °C to constant weight. For the samples which were to be freed from catalyst traces, after the reaction was stopped by addition of a small amount of ethanol, the polymerization mixture was washed thoroughly twice with dilute HCl, then with water, dilute $KHCO_3$, and again water, before precipitation of the polymer with pure ethanol. For run 10, two fractions were recovered as follows: after precipitation from the dichlorobenzene reaction mix using ethanol/HCl (300 cm^3), the polymer was collected by filtration, redissolved in hot toluene (100 cm^3), reprecipitated with pure ethanol (200 cm^3), and vacuum-dried (main fraction 10a, 8 g). The ethanol and toluene were evaporated under vacuum from the combined filtrates, and the dichlorobenzene containing the oligomeric fraction was washed, as described above, to remove aluminum, catalyst, and acid residues. After evaporation of all the solvent under vacuum, the oily residue was redissolved in pentane (20 cm^3) and filtered. To the pentane solution was added methanol (50 cm^3), and the pentane was evaporated in order to reprecipitate an oily wax, which was recovered from the pure methanol at 0 °C and vacuum-dried (oligomeric fraction 10b, 0.4 g).

NMR Analysis. ^1H and ^{13}C NMR spectra were recorded in pulsed Fourier transform mode at 270 and 67.89 MHz, respectively, on a Bruker 270 spectrometer in $C_2D_2Cl_4$ solution at 103 °C. Samples were prepared by dissolving 250 mg of sample in 2 cm^3 of solvent. Chemical shifts were referred to internal hexamethyldisiloxane [δ(HMDS) $\approx$ δ(TMS) $-$ 2.0 ppm for ^{13}C, δ(HMDS) $\approx$ δ(TMS) $-$ 0.06 ppm for ^1H]. For ^1H spectra, typically 500 free induction decays were accumulated. ^{13}C spectra were measured with composite pulse decoupling to remove $^{13}C-^1H$ couplings, the pulse angle was 90°, and the pulse repetition time was 27 s. ^{13}C DEPT NMR spectra were measured with composite pulse decoupling using the sequence $\tau_1-90°-\tau_2-180°$, $90°-\tau_2-135°$, $180°-\tau_2-$CPD$-$acquire, with delays τ_1 of 24 s, and τ_2 of 4.0 ms and 90° pulse widths of 10.1 μs and 18.0 μs for ^{13}C and ^1H, respectively. For both normal and DEPT ^{13}C spectra, windows of 13889 Hz were observed, accumulating 5000 free induction decays on 64 K of computer memory.

Acknowledgment. We thank Professor Umberto Giannini for his constant interest in this work and for many useful discussions. Financial help from the EC Project "Human Capital and Mobility", Network no. ERBCHGECT 930/58 OPTMO (Olefin Polymerization with Catalysts Based on Transition Metals and Organometallics), is gratefully acknowledged.

References and Notes

(1) Carvill, A.; Tritto, I.; Locatelli, P.; Sacchi, M. C. *Macromolecules* **1997**, *30*, 7056 and references therein.

(2) (a) Tsutsui, T.; Kashiwa, N.; Mizuno, A. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 565. (b) Kioka, M.; Mizuno, A.; Tsutsui, T.; Kashiwa, N. *ACS Symp. Series* **1992**, *496*, 72. (c) Kojoh, S.; Kioka, M.; Kashiwa, N.; Itoh, M.; Mizuno, A. *Polymer* **1995**, *36*, 5015. (d) Chadwick, J. C.; Miedema, A.; Sudmeijer, O. *Macromol. Chem. Phys.* **1994**, *195*, 167. (e) Chadwick, J. C.; van Kessel, G. M. M.; Sudjmeier, O. *Macromol. Chem. Phys.* **1995**, *196*, 14. (f) Chadwick, J. C.; Morini, G.; Albizzati, E.; Balbontin, G.; Mingozzi, I.; Cristofori, A.; Sudmeijer, O.; van Kessel, G. M. M. *Macromol. Chem. Phys.* **1996**, *197*, 2501. (g) Albizzati, E.; Giannini, U.; Balbontin, G.; Camurati, I.; Chadwick, J. C.; Dall'Occo, T.; Dubitsky, Y.; Galimberti, M.; Morini, G.; Maldotti, A. *J. Polym. Sci.*, in press. (h) Bukatov, G. D.; Gancharov, V. S.; Zakharov, V. A. *Makromol. Chem. Phys.* **1995**, *196*, 1751.

(3) (a) Hayashi, T.; Inoue, Y.; Chûjô, R.; Asakura, T. *Macromolecules* **1988**, *21*, 2675. (b) Imaoka, K.; Ikai, S.; Tamura, M.; Yoshikiyo, M.; Yano, T. *J. Mol. Catal.* **1993**, *82*, 37. (c) Busico, V.; Cipullo, R.; Chadwick, J. C.; Modder, J. F.; Sudjmeier, O. *Macromolecules* **1994**, *27*, 7538. (d) Jüngling, S.; Mülhaupt, R.; Stehling, U.; Brintzinger, H. H.; Fischer, D.; Langhauser, F. *J. Polym. Sci., Part A* **1995**, *33*, 1305.

(4) (a) Shiono, T.; Soga, K. *Macromolecules* **1992**, *25*, 3356. (b) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025. (c) Resconi, L.; Jones, R. L.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998. (d) Resconi, L.; Piemontesi, F.; Camurati, I.; Balboni, D.; Sironi, A.; Moret, M.; Rychlicki, H.; Ziegler, R. *Organometallics* **1996**, *15*, 5046. (e) Rieger, B.; Reinmuth, A.; Röll, W.; Brintzinger, H. H. *J. Mol. Catal.* **1993**, *82*, 67.

(5) Dolatkhani, M.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1995**, *196*, 3091.

(6) Couperus, P. A.; Clague, A. D. H.; van Dongen, J. P. C. M. *Org. Magn. Reson.* **1976**, *8*, 426.

(7) The polymerization at 100 °C was to be carried out in *o*-dichlorobenzene (DCB), which was chosen for its relatively low vapor pressure at this temperature. The polymerization at 60 °C has been performed in both toluene and DCB in order to ascertain that, at least qualitatively, the same chain-end groups are formed in both solvents. In fact the differences observed in the numbers of the chain-end groups are probably due to the different solubilities of the monomer in toluene and DCB at 60 °C.

(8) Schupfner, G.; Kaminsky, W. *J. Mol. Catal. A* **1995**, *C102*, 59.

(9) Forlini, F.; Fan, Z. Q.; Tritto, I.; Locatelli, P.; Sacchi, M. C. *Macromol. Chem. Phys.* **1997**, *198*, 2397.

(10) Busico, V.; Cipullo, R.; Boriello, A. *Macromol. Rapid Commun.* **1995**, *16*, 269.

(11) Prosenc, M. H.; Brintzinger, H. H. *Organometallics* **1997**, *16*, 3889.

(12) (a) Resconi, L.; Fait, A.; Piemontesi, F.; Colonnesi, M.; Rychlicki, H.; Ziegler, R. *Macromolecules* **1995**, *28*, 6667. (b) van der Burg, M. W.; Chadwick, J. C.; Sudmeijer, O.; Tulleken, H. J. A. *Makromol. Chem., Theory Simul.* **1993**, *2*, 399. (c) Rieger, B.; Reinmuth, A.; Röll, W.; Brintzinger, H. H. *J. Mol. Catal.* **1993**, *82*, 67.

(13) (a) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzochi, R. *Macromolecules* **1988**, *21*, 617. (b) Cheng, H. N.; Smith, D. A. *Macromolecules* **1986**, *19*, 2065. (c) Cheng, H. N. *Macromol. Symp.* **1994**, *86*, 77.

MA9800156