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Copolymerization of Ethylene with 4-Methyl-1,3-pentadiene Promoted by Titanium Complexes Containing a Tetradentate [OSSO]-Type Bis(phenolato) Ligand

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ABSTRACT: Copolymerization of ethylene with 4-methyl-1,3-pentadiene (4-MPD) catalyzed by 1,4-dithabutanediyl-linked bis(phenolato) titanium complexes **1** and **2** activated by methylaluminoxane (MAO) produced exclusively ethylene−4-MPD copolymers with high activity. The copolymer microstructure can be varied by changing the ratio between the monomers in the copolymerization feed, affording copolymers with 4-MPD content up to 83%. The resulting copolymer are crystalline as shown by thermal analysis and by the X-ray powder diffraction profiles. The microstructural features were fully elucidated by ^{13}C NMR spectroscopy revealing that the copolymers with various 4-MPD content show a strong tendency to the alternating microstructure which was confirmed by the kinetic elaboration.

Introduction

The synthesis of polyolefins containing functional groups along the chain backbone has attracted much attention in the past years.[1] In particular, the synthesis of polyolefins bearing pendant double bonds via the copolymerization of olefin with diene has been attracting increasing interest because of the possibility to easily convert the double bonds into functional groups, giving a broad range of polymers containing polar functionalities.[2]

However, the direct polymerization of ethylene with conjugated dienes often face difficulties due to the completely different behavior of the two classes of monomers for a given catalytic system that cause a lowering of the catalyst activity and a low incorporation of the comonomer in the resulting polymer.

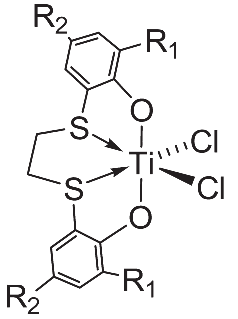
In order to circumvent this problem, many researchers have obtained good results by the copolymerization of ethylene with nonconjugated dienes[3] or with cyclic dienes.[4]

In this scenario, a monomer of potential interest for the synthesis of polymers having pendant double bonds along the polymer chain is 4-methyl-1,3-pentadiene (4-MPD). Indeed, the presence of an olefinic carbon atom bearing two methyl groups in the 4-MPD structure renders the behavior of this monomer in homopolymerization closer to styrene than to that of other dienes (e.g., 1,3-butadiene, isoprene).

As a matter of fact, among the six possible stereoregular polymers for this monomer, only the two stereoregular 1,2 structures are known so far.[5]

In particular, the polymerization of 4-methyl-1,3-pentadiene (4-MPD) to 1,2 syndiotactic polymer is promoted by many homogeneous catalytic systems consisting of titanium or zirconium compounds, soluble in aromatic hydrocarbons activated by methylaluminoxane (MAO).[6] Notably while many homogeneous catalytic systems promote the copolymerization of ethylene with styrene,[7] the copolymerization of ethylene by using monocyclopentadienyl titanium compounds activated by MAO results in low activity and, more importantly, a decrease of chemoselectivity which causes an increase of the 1,4 units respect to the 1,2 units.[8]

Scheme 1



1 $R_1 = R_2 = t\text{-Bu}$

2 $R_1 = C(CH_3)_2Ph\ R_2 = CH_3$

The synthesis of 1,2-isotactic poly(4-MPD) has been performed by using various heterogeneous catalysts,[9] but only recently we found an efficient and stereoselective homogeneous titanium system which incorporates a tetradentate ligand having two phenolate units linked through a 1,ω dithiaalkanediyl bridge $S(CH_2)_2S$.[10] Notably this system has shown to stereoselectively homopolymerize butadiene to *trans*-1,4-polybutadiene[11] and efficiently copolymerize ethylene with styrene[12] and butadiene.[13]

We report herein the ability of two catalytic systems based on 1,4-dithiabutanediyl bridged phenols (Scheme 1) to efficiently copolymerize ethylene with 4-MPD giving, under acceptable experimental conditions, a polymer with alternating microstructure.

Experimental Part

Materials. All manipulations of air- and/or water-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques or a MBraun glovebox. Commercial grade toluene (Carlo Erba) was dried over calcium chloride, refluxed 48 h under a nitrogen atmosphere over sodium, and distilled before using. Polymerization grade

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Table 1. Ethylene−4-Methyl-1,3-pentadiene Polymerization Results

run[a]	catalyst	4-MPD in the feed (mol %)	yield (g)	activity[b]	4-MPD in the polymer (mol %)	T_g (°C)	T_m (°C)	$M_n/10^3$	M_w/M_n
1	**1**	83	1.33	133	51	−17.2	98.14	6.4	1.59
2	**1**	78	2.98	298	46	−25.9	99.38	6.2	1.62
3	**1**	74	2.85	285	49	−25.7	98.67	6.9	1.61
4	**1**	65	2.30	230	43	−26.8	108.7	7.1	1.59
5	**1**	59	1.70	170	40	−28.1	110.5	6.9	1.55
6	**1**	50	2.56	128	22	−32.6	115.5	4.9	1.78
7	**1**	49	1.69	179	17	−33.6	115.6	6.8	1.44
8	**1**	33	1.79	169	7.9	−37.9	115.4	6.3	1.31
9	**2**	83	4.11	411	83	2.40	85.30	104.2	1.63
10	**2**	78	3.33	333	73	1.80	98.40	125.4	1.36
11	**2**	71	2.69	269	71	−3.10	102.8	40.0	2.11
12	**2**	59	1.39	139	51	−15.1	103.9	15.4	1.86
13	**2**	49	0.99	99.0	44	−19.6	108.5	11.4	1.83
14	**2**	40	0.60	60.0	40	−24.2	108.6	10.4	1.69

[a] Polymerization conditions: Ti complex (10.0 μmol), Al/Ti = 1200, toluene (10 mL), ethylene pressure = 1 atm, polymerization time: 1 h. [b] Activity = kg/(mol Ti)·h.

ethylene, purchased from Società Ossigeno Napoli (S.O.N.), was dried by passing through a column filled with activated molecular sieves (4 Å). 4-Methyl-1,3-pentadiene was synthesized according to a literature procedure[14] and purified by distillation over calcium hydride under a nitrogen atmosphere. Methylalumoxane (MAO), purchased from Aldrich as a 10 wt % solution in toluene, was dried in vacuo at 50 °C to remove toluene and "free" $AlMe_3$ and used as a solid after washing hexane. The titanium complexes **1** and **2** were prepared according to the literature procedures.[15,16]

Copolymerization of Ethylene and 4-Methyl-1,3-pentadiene. The copolymerization runs were carried out following a standard procedure. A 100 mL flask equipped with a magnetic bar was charged with 0.70 g of MAO (0.01 mol, Al/Ti = 1200), and the proper amount of a 4-methyl-1,3-pentadiene solution in toluene, to reach a total volume of 10 mL. The flask was then evacuated and filled with ethylene (1 atm); after equilibration of the solution at target temperature the reaction was started by injection of a toluene solution (1 mL) of the catalyst (10 μmol). The run was terminated after the desired time by introducing ethanol (15 mL) and antioxidant (Wingstay K; 0.5−0.75 phr). The polymer was coagulated in ethanol (200 mL) acidified with aqueous HCl, recovered by filtration, washed with an excess of ethanol, and dried in vacuo at room temperature.

Hydrogenation of Ethylene−4-Methyl-1,3-pentadiene Copolymer. A sample (1 g) of the copolymer (containing 22% of 4-MPD (run 5, Table 1) was dissolved in toluene (75 mL), *p*-toluensulfonylhydrazine was added (8 g), and the resulting mixture was refluxed for 48 h under stirring. The reaction was stopped by quenching with ethanol (200 mL), and the resulting polymer was recovered by filtration, washed with water and ethanol, and dried in vacuo until constant weight.

Characterization of the Polymers. The ^{13}C NMR spectra of the ethylene−4-MPD copolymers samples were recorded with a Bruker AVANCE 300 spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C). Using 5 mm (o.d.) NMR tubes, polymer samples (30 mg) were dissolved in tetrachloroethane-d_2 (0.7 mL) and analyzed at 363 K. Chemical shifts were referenced to TMS and calculated by using the residual isotopic impurities of the deuterated solvent (74.26 ppm for tetrachloroethane-d_2). The monomer compositions of the copolymer ethylene−4-MPD samples were determined by comparing the integrals of the ^{13}C resonances by using the following formula in analogy to ethylene−styrene copolymers:[17]

$$\begin{aligned} 4\mathrm{MPD} &= I_{(\mathrm{S}\alpha\alpha)} + I_{(\mathrm{S}\alpha\beta)}/2 + I_{(\mathrm{S}\alpha\gamma)}/2 \\ \mathrm{E} &= I_{(\mathrm{S}\beta\beta)} + I_{(\mathrm{S}\beta\boldsymbol{\delta})}/2 + I_{(\mathrm{S}\gamma\boldsymbol{\delta})}/2 \end{aligned}$$

The thermal analysis of the polymers was carried out on TA Instrument DSC 2920 using a heating rate of 10 °C min^{-1}.

The average molecular weights of the polymer samples were determined at 30 °C with a 150C Waters GPC equipped with JASCO 875-UV (254 nm) and WGE-DR BURES ETA1002 refractive index detectors and three PSS columns set consisting of 10^5, 10^4, and 100 Å (pore size)−5 μm (particle size) column. $CHCl_3$ was used as carrier solvent with a flow rate of 1.0 mL/min. The calibration curve was established with polystyrene standards.

Wide-angle X-ray powder diffraction (WAXD) profiles were collected at room temperature, with an automatic 1710 Philips diffractometer using Ni-filtered Cu Kα radiation (λ = 1.5418 Å) and scans in the 2θ range 4°−40°.

Results and Discussion

The performances of **1**/MAO and **2**/MAO in ethylene−4MPD polymerization were explored under different experimental conditions: the main results are summarized in Table 1.

The catalysts show good activity under the polymerization conditions used, and notably no dramatic lowering of the catalyst activity by increasing the 4-MPD concentration in the feed is observed. In particular, the activity of the catalyst **1** does not vary significantly with 4-MPD content in the feed while the catalyst **2** increases the activity by increasing the 4-MPD content in the feed. One can also observe that the catalyst **2** incorporates more efficiently the 4-MPD in the polymer, resulting in copolymers with high content of 4-MPD (up to 83%). The T_g values increase by increasing the 4-MPD content varying from −37.9 to 2.4 °C while the melting temperatures increase by increasing the ethylene content in the copolymer from 85.3 to 115.6 °C. Moreover, the X-ray powder diffraction profile of the as-prepared copolymer sample containing 43% mol of 4-MPD (run 4) evidences that the sample is crystalline and that it crystallizes in a new crystalline form different from the crystalline form[18] of polyethylene and different from that of 1,2-isotactic poly(4-MPD).[9a,10] The molecular weight of the polymers does not vary significantly in the range of composition explored for the catalyst **1** while increase of 1 order of magnitude for the catalyst **2** increasing the 4-MPD content from 40% to 83%. The molecular weight distributions are monomodal for both systems ranging between 1.31 and 2.11, indicating a single-site catalyst and the material being copolymeric in nature. In addition, efforts to fractionate the polymer in common organic solvents (acetone, hexane, ethyl acetate, THF) were unsuccessful.

A deeper insight into the microstructural features of the copolymers was achieved by using ^{13}C NMR spectroscopy. In contrast to the copolymer obtained in presence of monocyclopentadienyl titanium complexes,[8] 4-MPD is exclusively inserted in 1,2 fashion (or 2,1) and no 1,4 units are detectable by the

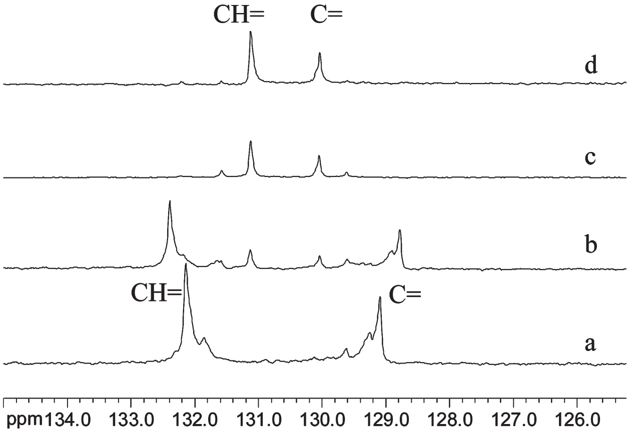


Figure 1. Olefinic region of the ^{13}C NMR spectra of ethylene−4-MPD copolymers prepared with catalysts **1** and **2** activated by MAO:1,2 isotactic poly(4-MPD) (a), 83% 4-MPD (run 9, Table 1) (b), 51% 4-MPD (run 1, Table 1) (c), and 22% 4-MPD (run 6, Table 1) (d).

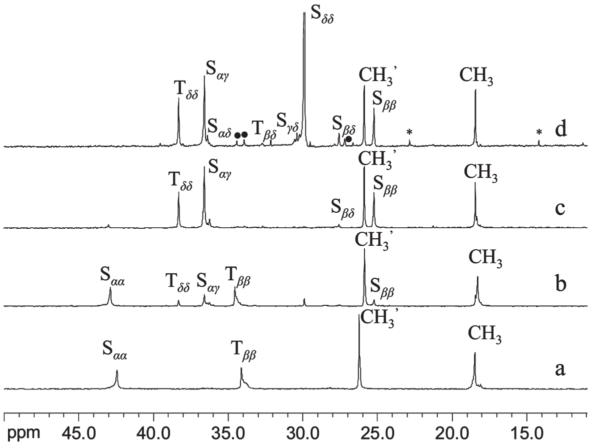


Figure 2. Aliphatic region of the ^{13}C NMR spectra of ethylene−4-MPD copolymers prepared with catalysts **1** and **2** activated by MAO:1,2 isotactic poly(4-MPD) (a), 83% 4-MPD(run 9, Table 1) (b), 51% 4-MPD (run 1, Table 1) (c), and 22% 4-MPD (run 6, Table 1) (d). For the minor peaks (∗; ●) see ref 22.

Scheme 2

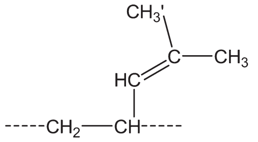
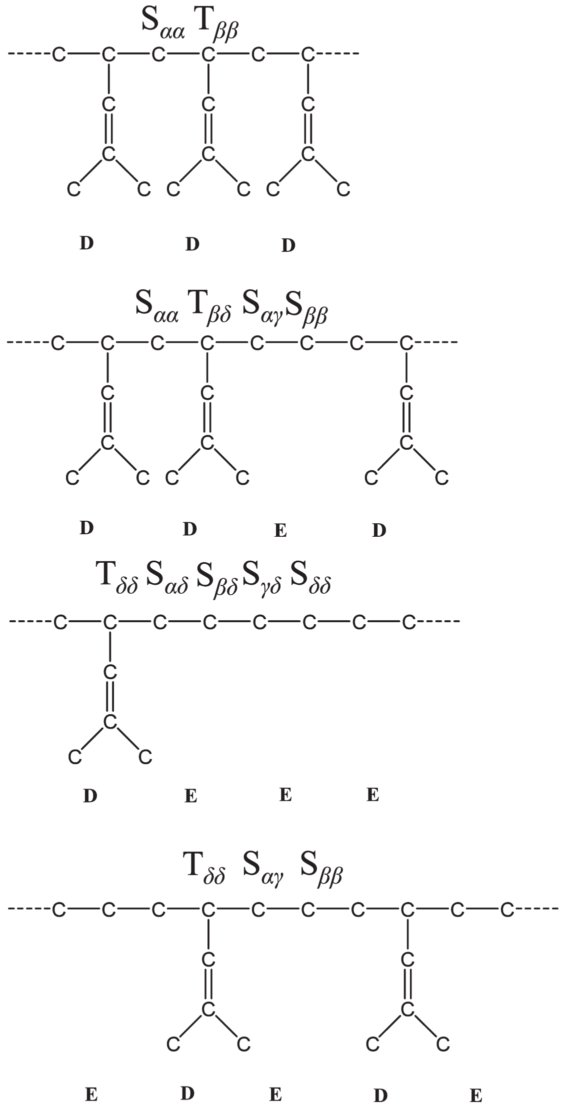


Table 2. ^{13}C NMR Assignments for the Ethylene−4-Methyl-1,3-pentadiene Copolymers

carbon type[a]	chemical shift (ppm)	sequence[b]
CH_3	18.42−18.47	DDD/EDE
$S_{\beta\beta}$	25.21	EDEDE
CH_3'	25.86−26.23	DDD/EDE
$S_{\beta\delta}$	27.55	DEE
$S_{\delta\delta}$	29.89	EEE
$S_{\gamma\delta}$	30.38	DEEE
$T_{\beta\delta}$	32.68	DDE
$S_{\alpha\alpha}$	34.12	DDD
$S_{\alpha\delta}$	36.36	DEE
$S_{\alpha\gamma}$	36.57	EDEDE
$T_{\delta\delta}$	38.30	EDE
$T_{\delta\delta}$	42.44	DDD
C=	129.0−130.0	DDD/EDE
CH=	131.1−132.1	EDE/DDD

[a] See Schemes 2 and 3. [b] D = 4-methyl-1,3-pentadiene unit; E = ethylene unit.

Scheme 3



analysis of the olefinic region. In addition, one can observe from the spectra of the copolymer at different composition and that of isotactic poly(4-MPD) that the signals relative to the olefinic carbon atom bearing the two methyl groups in the side chain and the olefinic methine carbon at 129.0 and 132.1 ppm, respectively, in the homopolymer (DDD sequences in Scheme 2) shift in the alternate sequences with ethylene respectively at 130.0 and 131.1 ppm (EDE sequences)[19](see Figure 1).

In Figure 2, the aliphatic region of the spectra of isotactic poly(4-MPD) (a) and the copolymers containing 83% (b), 51% (c), and 22% (d) of comonomer moles is shown.

The carbon terminology follows that of Carman and Wilkes,[20] where S, T, and P refer respectively to the secondary (methylene), tertiary (methine), and primary (methyl) carbons of the main chain. The position of a carbon relative to its nearest T groups was labeled by two Greek subscripts where δ indicates all T carbons four bond away and δ+ those which are farther than four bonds from the S carbon of interest. The methyl groups of the side chain are indicated with CH_3 and CH_3' as in Scheme 2.

The assignments have been made by comparing the spectra not only with different 4-MPD content but also with DEPT experiment which allowed us to unequivocally distinguish methyl, methylene, and methine carbons.[21]

The assignments are listed in Table 2, and the relative sequences are shown in Scheme 3.

It is worth noting the strong tendency of both the catalysts to produce alternating ethylene−4-MPD sequences even in the copolymers with low comonomer content as evidenced by the presence of the $S_{\beta\beta}$ methylene carbon relative to the alternating sequences in the sample with only 22% of 4-MPD.[22] The isoselectivity of the catalysts in the 4-MPD homopolymerization and the similar behavior of this monomer to styrene can suggest that the stereoselectivity is retained in the copolymerization analogously to that observed in ethylene−styrene copolymerization.[12]

A further confirmation of the chemical shift assignments has been obtained by hydrogenation of the copolymer with 22% of 4-MPD. The spectra of the original ethylene−4-MPD copolymer (a) and the resulting ethylene−4-methyl-1-pentene copolymer (b) are shown in Figure 3.

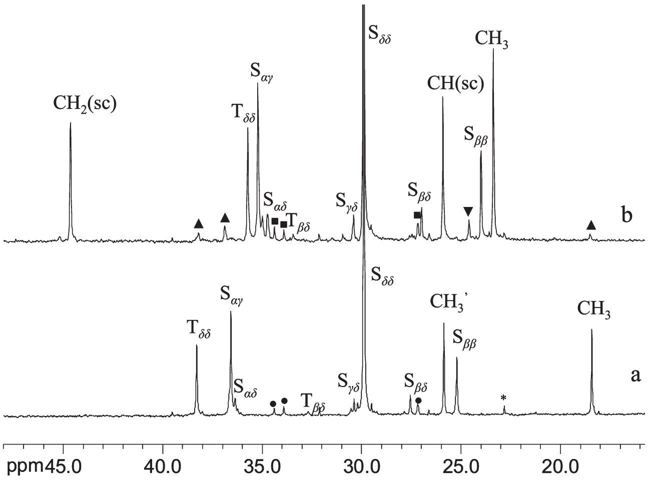
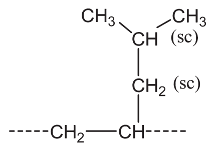


Figure 3. Aliphatic region of the ^{13}C NMR spectra of ethylene−4-MPD copolymer prepared with catalysts **1**/MAO:22% 4-MPD (run 6, Table 1) (a) and the same sample after hydrogenation (b). For the minor peaks (∗, ●, ▼, ▲, ■) see refs 22 and 24.

Scheme 4



One can observe that the same sequences are present in both the copolymers with the chemical shift of the resulting ethylene−4-methyl-1-pentene well in agreement with data reported in the literature for the copolymers containing alternating sequences.[23] For comparison, the chemical shift and the relative sequences before and after the hydrogenation are listed in Table 3.[22,24]

The reactivity ratios $r_1 = k_{EE}/k_{DE}$ and $r_2 = k_{DD}/k_{ED}$ for ethylene−4-MPD copolymerization catalyzed by **1**/MAO and **2**/MAO were also evaluated. As the 4-MPD insertion is exclusively 1,2 (or 2,1) specific, a binary copolymerization scheme and the terminal model in which only the last inserted monomer units at the active catalyst site influence the propagation reaction were assumed.

To minimize the composition drift, the copolymerization reactions were stopped after 5 min, corresponding to a monomer conversion of 5−7%. The reactivity ratios obtained from the Fineman−Ross[25] plots are $r_1 = 1.12 \pm 6.0 \times 10^{-4}$ and $r_2 = 0.05 \pm 1.6 \times 10^{-2}$ for the catalyst **1** and $r_1 = 0.55 \pm 2.4 \times 10^{-3}$ and $r_2 = 0.28 \pm 7.1 \times 10^{-3}$ for **2**. These values indicate a preference for insertion of ethylene vs 4-MPD when the last inserted monomer unit in the growing polymer chain is ethylene for both catalytic systems. On the other hand, the reactivity versus 4-MPD is also quite high and comparable to those reported for ethylene−styrene[12] and ethylene−butadiene[13] copolymerization for the catalytic system **1**. The products of the reactivity ratios ($r_1r_2 = 0.05 \pm 1.6 \times 10^{-2}$ for **1** and $r_1r_2 = 0.15 \pm 4.4 \times 10^{-3}$ for **2**) indicate a tendency of the monomers to form alternating copolymers, in agreement with the microstructure determined by ^{13}C NMR analysis.

Conclusions

To the best of our knowledge, **1**/MAO and **2**/MAO are the first homogeneous titanium catalysts active in ethylene−4-MPD copolymerization under reasonable experimental conditions affording prevailingly alternating copolymers. This new polymeric material has been fully characterized and its microstructure completely elucidated by means of ^{13}C NMR spectroscopy. These results confirm that this class of catalyst is a powerful tool for the synthesis of new polyolefinic materials with unprecedented molecular architectures. In addition, the presence of pendant reactive double bonds along the polymer backbone opens the possibility to introduce polar functionality under mild reaction conditions. Further work is in progress in order to selectively functionalize the pendant double bonds of the

Table 3. ^{13}C NMR Assignments for the Ethylene−4-Methyl-1,3-pentadiene Copolymer Containing 22% of 4MPD and the Corresponding Hydrogenated Copolymer Ethylene−4-Methyl-1-pentene

carbon type[a]	chemical shift (ppm)[b]	polymer sequence[c]	chemical shift observed (ppm)[d]	chemical shift expected (ppm)[e]	polymer sequence[f]
CH_3	18.47	EDE	23.40	23.28	EPE
$S_{\beta\beta}$	25.21	EDEDE	24.00	23.90	EPEPE
CH_3'	26.23	EDE			
CH(sc)			25.92	25.85	EPE
$S_{\beta\delta}$	27.55	DEE	26.99	26.91	PEE
$S_{\delta\delta}$	29.89	EEE	29.91	29.83	EEE
$S_{\gamma\delta}$	30.38	DEEE	30.41	30.36	PEEE
$T_{\beta\delta}$	32.68	DDE	33.44	33.38	PEE
$S_{\alpha\delta}$	36.36	DEE	34.74	34.64	PEE
$S_{\alpha\gamma}$	36.57	EDEDE	35.22	34.94−35.54	EPEPE
$T_{\delta\delta}$	38.30	EDE	35.73	35.73	EPE
CH_2(sc)			44.64	44.60	EPE

[a] The carbon atoms are labeled following the Schemes 2, 3, and 4. For the hydrogenated sample the only difference is the absence of the double bond in the side chain. [b] Chemical shift observed for the ethylene−4-methyl-1,3-pentadiene copolymer (run 5, Table 1). [c] D = 4-methyl-1,3-pentadiene unit; E = ethylene unit. [d] Chemical shift observed for the ethylene−4-methyl-1-pentene copolymer obtained by hydrogenation of the ethylene−4-methyl-1,3-pentadiene copolymer (run 5, Table 1). [e] To facilitate the comparison, the chemical shifts from the literature[21] were reported in TMS scale using the following relation: δ(TMS) = δ(HMDS) + 2.1. [f] P = 4-methyl-1-pentene unit; E = ethylene unit.

copolymer and to clarify the crystalline structure of these new alternating ethylene−4-MPD copolymers.

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Supporting Information Available: ^{13}C NMR spectra of the copolymers and X-ray diffraction pattern of the copolymer sample containing 43% of 4-MPD (run 4, Table 1). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479–1494. (b) Chung, T. C. *Prog. Polym. Sci.* **2002**, *27*, 39–85. (c) Boaen, N. K.; Hillmyer, M. A. *Chem. Soc. Rev.* **2005**, *34*, 267–275. (d) Nomura, K.; Kitiyanan, B. *Curr. Org. Synth.* **2008**, *5*, 217–226.

(2) (a) Lu, B.; Chung, T. C. *Macromolecules* **1998**, *31*, 5943–5946. (b) Lu, B.; Chung, T. C. *Macromolecules* **1999**, *32*, 2525–2533. (c) Dong, J. Y.; Chung, T. C. *Macromolecules* **2002**, *35*, 2868–2870. (d) Dong, J. Y.; Manias, E.; Chung, T. C. *Macromolecules* **2003**, *36*, 3439–3447. (e) Dong, J. Y.; Hong, H.; Chung, T. C.; Wang, H. C.; Datta, S. *Macromolecules* **2003**, *36*, 6000–6009.

(3) (a) Naga, N.; Shiono, T.; Ikeda, T. *Macromol. Chem. Phys.* **1999**, *200*, 1466–1472. (b) Nomura, K.; Hatanaka, Y.; Okumura, H.; Fujiki, M.; Hasegawa, K. *Macromolecules* **2004**, *37*, 1693–1695. (c) Nomura, K.; Takemoto, A.; Hatanaka, Y.; Fujiki, M.; Okumura, H.; Hasegawa, K. *Macromolecules* **2006**, *39*, 4009–4017. (d) Nomura, K.; Liu, J.; Fujiki, M.; Takemoto, A. *J. Am. Chem. Soc.* **2007**, *129*, 14170–14171. (e) Lin, W.; Shao, Z.; Dong, J.-Y.; Chung, T. C. *Macromolecules* **2009**, *42*, 3750–3754.

(4) (a) Suzuki, J.; Kino, Y.; Uozumi, T.; Sano, T.; Teranishi, T.; Jin, J.; Soga, K.; Shiono, T. *J. Appl. Polym. Sci.* **1999**, *72*, 103–108. (b) Radhakrishnan, K.; Sivaram, S. *Macromol. Chem. Phys.* **1999**, *200*, 858–862. (c) Mönkkönen, K.; Pakkanen, T. T. *Macromol. Chem. Phys.* **1999**, *200*, 2623–2628. (d) Williamson, A.; Fink, G. *Macromol. Chem. Phys.* **2003**, *204*, 195–202. (e) Li, X. F.; Hou, Z. M. *Macromolecules* **2005**, *38*, 6767–6769. (f) Heiser, D. E.; Okuda, J.; Gambarotta, S.; Mulhaupt, R. *Macromol. Chem. Phys.* **2005**, *206*, 195–202. (g) Li, X. F.; Baldamus, J.; Nishiura, M.; Tardif, O.; Hou, Z. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 8184–8188. (h) Pan, L.; Ye, W.-P.; Liu, J. Y.; Hong, M.; Li, Y.-S. *Macromolecules* **2008**, *41*, 2981–2983.

(5) (a) Porri, L.; Giarrusso, A. In *Comprehensive Polymer Science*; Pergamon Press: Oxford, U.K., 1989; Vol. *4*, pp 53−108. (b) Proto, A.; Capacchione, C. In *Stereoselective Polymerization with Single-Site Catalysts*; Baugh, L.S., Canich, J. A. M., Eds.; CRC Press: Boca Raton, FL, 2008; pp 445−473.

(6) (a) Zambelli, A.; Ammendola, P.; Proto, A. *Macromolecules* **1989**, *22*, 2126–2128. (b) Oliva, L.; Longo, P.; Grassi, A.; Ammendola, P.; Pellecchia, C. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 519–521. (c) Longo, P.; Proto, A.; Oliva, P.; Zambelli, A. *Macromolecules* **1996**, *29*, 5500–5501. (d) Ricci, G.; Porri, L. *Polymer* **1997**, *38*, 4499–4503. (e) Pragliola, S.; Forlenza, E.; Longo, P. *Macromol. Rapid Commun.* **2001**, *22*, 783–786.

(7) (a) Pellecchia, C.; Oliva, L. *Rubber Chem. Technol.* **1999**, *72*, 553–558. (b) Rodrigues, A. S.; Carpentier, J. F. *Coord. Chem. Rev.* **2008**, *252*, 2137–2154.

(8) (a) Longo, P.; Grisi, F.; Proto, A.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1997**, *18*, 183–190. (b) Cugini, C.; Rombolà, O. A.; Giarrusso, A.; Porri, L.; Ricci, G. *Macromol. Chem. Phys.* **2005**, *206*, 1684–1690.

(9) (a) Porri, L.; Gallazzi, M. C. *Eur. Polym. J.* **1966**, *2*, 189–198. (b) Natta, G.; Corradini, P.; Bassi, I. *Eur. Polym. J.* **1968**, *4*, 297–315.

(10) Proto, A.; Capacchione, C.; Venditto, V.; Okuda, J. *Macromolecules* **2003**, *36*, 9249–9251.

(11) Milione, S.; Cuomo, C.; Capacchione, C.; Zannoni, C.; Grassi, A.; Proto, A. *Macromolecules* **2007**, *40*, 5638–5643.

(12) Capacchione, C.; Proto, A.; Ebeling, H.; Mulhaupt, R.; Okuda, J. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1908–1913.

(13) Capacchione, C.; Avagliano, A.; Proto, A. *Macromolecules* **2008**, *41*, 4573–4575.

(14) Bachman, G. B.; Goebel, C. G. *J. Am. Chem. Soc.* **1942**, *64*, 787–790.

(15) Capacchione, C.; Proto, A.; Ebeling, H.; Mulhaupt, R.; Spaniol, T. P.; Möller, K.; Okuda, J. *J. Am. Chem. Soc.* **2003**, *125*, 4964–4965.

(16) Capacchione, C.; Manivannan, R.; Barone, M.; Beckerle, K.; Centore, R.; Oliva, L.; Proto, A.; Tuzi, A.; Spaniol, T. P.; Okuda, J. *Organometallics* **2005**, *24*, 2971–2982.

(17) Proto, A.; Senatore, D. *Macromol. Chem. Phys.* **1999**, *200*, 1961–1964.

(18) See Supporting Information.

(19) In the ^{13}C NMR spectra of the copolymers obtained with catalyst **1**/MAO a signal at 120.69 ppm (see Supporting Information), which is probably due to unsaturated chain end due to undesired β-hydrogen transfer to the metal center.

(20) Carman, C. J.; Wilkes, C. E. *Rubber Chem. Technol.* **1971**, *44*, 781–804.

(21) See Supporting Information.

(22) In the spectrum of the polymer containing the highest ethylene content (22% 4-MPD) (d) the peaks at 14.14 and 22.80 ppm marked with an asterisk are relative to methyl carbon atoms belonging to the polymer chain ends arising from the initiation step on the Ti−CH$_3$ bond and on the Ti−H bond, respectively (see ref 6c). The peaks marked with (●) are probably relative to the methylene carbon atoms belonging to the $S_{\beta\delta+}$ sequences (27.16 ppm) and $S_{\alpha\delta+}$ (33.89 and 34.36 ppm).

(23) Losio, S.; Boccia, A. C.; Sacchi, M. C. *Macromol. Chem. Phys.* **2008**, *209*, 1115–1128.

(24) In spectrum (b) the peaks marked with (▲) are clearly due to the presence of non-hydrogenated units. The peak marked with (▼) is also a methylene $S_{\beta\beta}$ carbon probably due to carbon atoms between hydrogenated and non-hydrogenated sequences. The peaks marked with (■) are relative to the corresponding sequences $S_{\beta\delta+}$ (27.18 ppm) and $S_{\alpha\delta+}$ (33.90 and 34.38 ppm) present in the non-hydrogenated sample.

(25) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 259–262.