

Homo-, co- and terpolymerization of 1,5-hexadiene using a methylalumoxane activated mono-Cp-amido-complex

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Summary

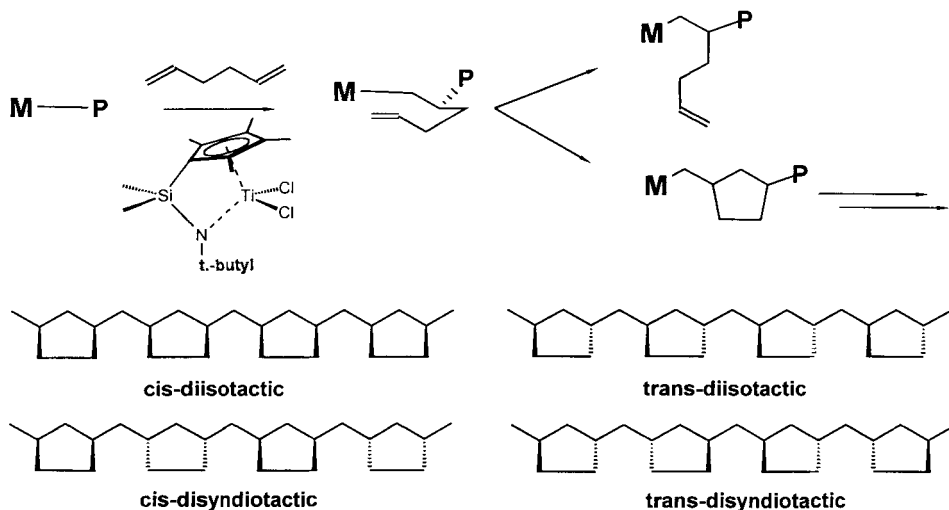
Homo- and copolymerizations of 1,5-hexadiene with ethene and styrene using halfsandwich metallocene catalyst $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N-tert-butyl})\text{TiCl}_2$ / MAO (Cp = cyclopentadienyl, Me = methyl, MAO = methylalumoxane) were investigated. According to ^{13}C -NMR spectroscopic microstructure analysis, cyclopolymerization of 1,5-hexadiene afforded randomly distributed cis- and trans-cyclopentane rings in the homo- and copolymer backbone. 1,5-hexadiene incorporation reached 52 mol-%. The ratio of vinyl side chains to cyclopentane rings was controlled by 1,5-hexadiene concentration, where low 1,5-hexadiene concentration promoted cyclopolymerization. Copolymer glass transition temperatures increased with increasing content of cyclic units in the backbone. Styrene was used successfully as comonomer in ethene/1,5-hexadiene polymerization, resulting in a semicrystalline terpolymer with cyclic and styrenic units in the polymer backbone.

Introduction

In contrast to conventional heterogeneous Ziegler-Natta systems metallocenes are capable to induce the polymerization and copolymerization of cyclic olefins (1,2,3) without inducing any ring-opening metathesis reaction (4). Cycloolefin copolymers (COC) are attractive materials, useful as compact disk substrate or engineering resin (5). A drawback of ethene copolymerization with cyclopentane is the low reactivity of cyclopentane with respect to that of ethene. Therefore, metallocene catalyzed cyclopolymerization of 1,5-hexadiene (6) represents an attractive synthetic route to cycloolefin copolymers (Scheme 1). Moreover, 1,5-hexadiene polymerization also permits incorporation of vinyl side chains.

Different catalytic systems have been introduced recently to polymerize 1,5-hexadiene (7,8,9). As shown in Scheme 1, cyclopolymerization affords cis- and trans-cyclopentane configurations. Stereoregular cyclopolymerization comprises a sequence of cyclopentanes with identical (diisotactic) or alternating (disyndiotactic) conformation of either cis- or trans-rings (Scheme 1).

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Scheme 1 Polymerization of 1,5-hexadiene and stereoregular configurations of poly(1,5-hexadiene)

The recent development of halfsandwich metallocenes of the mono-Cp-amido type (10,11) provides new opportunities in metallocene catalysis, especially in ethene copolymerization including 1-olefins as well as styrenic comonomers (11,12). Purpose of this research was to investigate homo- and copolymerization behavior of halfsandwich metallocenes such as $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N-tert-butyl})\text{TiCl}_2$ / MAO in order to control polymer microstructure. We also report terpolymerization of 1,5-hexadiene with ethene and styrene to prepare novel copolymers with cyclic and styrenic units in the backbone.

Experimental

Catalyst synthesis. The complex $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N-t-butyl})\text{TiCl}_2$ was synthesized according to the literature (10,11,12).

Materials. All manipulations involving air and moisture sensitive compounds were carried out under dry argon atmosphere, using Schlenk tube and glove box techniques. Methylalumoxane (MAO) was provided by Witco GmbH as 10 wt.-% solution in toluene. Toluene (Roth, p.a., >99,7%) was purified by passing it through a column with acidic Al_2O_3 , distilled over LiAlH_4 and refluxed over Na/K alloy, from which it was freshly distilled prior to use. Ethene was supplied by GHC Gerling, Holz & Co. Handels GmbH. Styrene (Fluka, > 99%) and 1,5-hexadiene (Aldrich, > 98%) were purified by distillation over LiAlH_4 and stored under argon at 0°C.

Copolymerizations. Copolymerizations were carried out in a 500 ml glass autoclave (Büchi AG, Uster/CH) for copolymerizations with ethene and in a 100 ml Schlenk-flask for polymerizations using only liquid monomers. The reactor/flask was filled with toluene, styrene/1,5-hexadiene and part of the methylalumoxane (MAO) needed. After thermostating, argon was removed via vacuo and the reaction mixture saturated with ethene. The metallocene solution (in 10 wt.-% MAO-solution) was then injected into the

reactor/flask, so that an in-situ-start of the copolymerization was achieved. Ethene pressure was kept constant during the polymerization. Further polymerization conditions are reported with Table 1. Copolymerizations were stopped by injecting C_3H_7OH and venting off excess of ethene. The copolymers were precipitated by pouring into 1 l of acidic (10 ml halfconc. HCl) CH_3OH , filtered and dried under vacuum to constant weight. *Characterization.* NMR spectra were recorded on a Bruker ARX 300 spectrometer operating at 300 MHz for 1H and at 75,4 MHz for ^{13}C . Spectra were taken at 100°C using $C_2D_2Cl_4$ as solvent. The chemical shifts are reported in ppm versus tetramethylsilane (TMS). Signals were assigned according to the literature (6,12). Molecular weights and molecular weight distributions reported were determined by gel permeation chromatography (GPC) versus polystyrene standard. Differential scanning calorimetry (DSC) was performed on a Perkin Elmer DSC-4 thermal analyser using a heating rate of 20°/min in the second heating.

Results and discussion

Homopolymerization. Results of the homopolymerization of 1,5-hexadiene by means of $Me_2Si(Me_4Cp)(N-t-butyl)TiCl_2/MAO$ at temperatures from 0°C to 60°C are summarized in Table 1.

Table 1

Homopolymerization of 1,5-hexadiene using $Me_2Si(Me_4Cp)(N-t-butyl)TiCl_2/MAO^a)$

run	T [°C]	1,5-HD conc. [mol/l]	yield [g]	activity ^{c)}	cis/trans- ratio	M_n [kg/mol]	M_w/M_n	T_g [°C]	T_m [°C]	uncyclised monomers [%]
1	20	0,42	1,0	74	47:53	49	4,1	51	-	< 5
2	60	0,42	1,1	82	48:52	49	2,9	55	-	< 5
3	0	0,42	1,0	74	48:52	52	2,7	51	-	< 5
4	20	0,84	1,3	48	48:52	67	6,0	47	-	< 5
5 ^{b)}	20	2,10	2,8	17	51:49	d)	d)	34	-	22

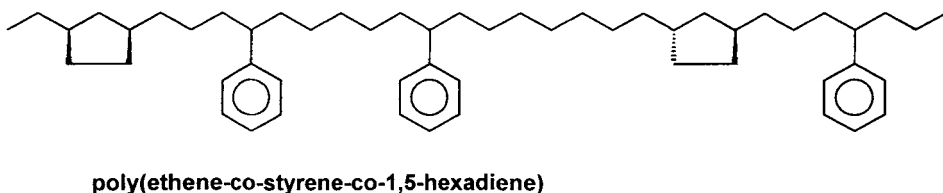
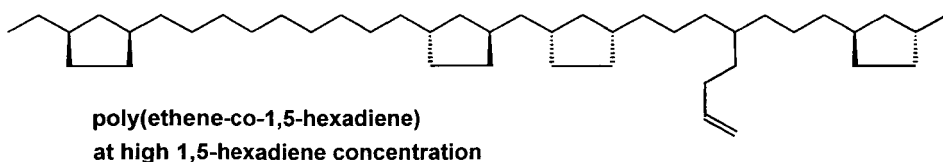
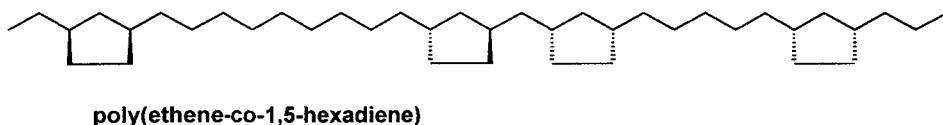
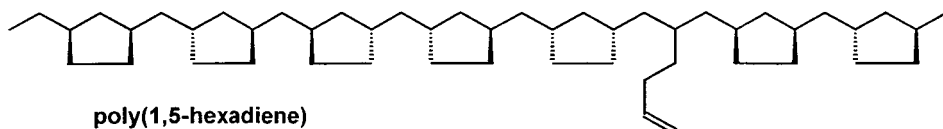
a) Polymerization conditions: [cat] = 80 $\mu mol/l$, Al:Ti = 1000, t = 4 h b) [cat] = 100 $\mu mol/l$, Al:Ti = 2000, t = 8 h c) activity in g polymer / (mol Ti * h * (monomer concentration in mol/l)) d) insoluble in high-temperature GPC, probably due to crosslinking reactions of uncyclised olefins (7)

Catalyst activity, taking into account monomer concentration, decreased with increasing monomer concentration. Also the amount of uncyclized monomeric units increased with monomer concentration. Obviously, there is a competition between intramolecular cyclization and insertion of 1,5-hexadiene. Most likely, lower insertion rate for the later could explain decreasing activity with increasing monomer concentration. Compared to other catalytic systems (6a,6b) $Me_2Si(Me_4Cp)(N-t-butyl)TiCl_2/MAO$ produces homopolymers of relatively high molecular mass with $M_n = 50.000$ g/mol and $M_w = 150.000$ g/mol, as determined by SEC using polystyrene standards. The polydispersity was in the range of $M_w/M_n = 2$ to 3 for polymers produced at low monomer

concentrations but increased with monomer concentration and with the amount of uncyclized monomeric units. Different polymerization conditions (temperature, monomer concentration, catalyst concentration) did not influence polymer microstructure. For all polymers a random distribution of approximately 1:1 for the ratio of cis- to trans-rings was observed.

Homopolymers with low amount of vinyl side chains are amorphous with a glass transition temperature (T_g) of about 50°C. This glass transition temperature is significantly reduced with increasing amount of vinyl side chains as can be seen for the polymer produced in run 5 with $T_g = 34^\circ\text{C}$. The amount of uncyclized units is usually well below 5 mol-%. This amount increases rapidly at concentrations higher than 10 vol-% 1,5-hexadiene. With a monomer concentration of 2,10 mol/l it was possible to introduce 22 mol-% of vinyl side chains (run 5). At 135°C in solution crosslinking of polymers occurred. High vinyl content is interesting for reactive processing applications such as dynamic vulcanization or for functionalization.

Co- and terpolymerization. Scheme 2 shows the co- and terpolymerizations possible for 1,5-hexadiene with ethene and styrene as comonomers using $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N-t-butyl})\text{TiCl}_2/\text{MAO}$ catalyst. Table 2 summarizes the results of the copolymerizations.



Scheme 2 Microstructures of homo-, co- and terpolymers of 1,5-hexadiene

Table 2 Co- and terpolymerization of 1,5-hexadiene with styrene and ethene using Me₂Si(Me₄Cp)(N-t-butyl)TiCl₂/MAO^{a)}

run	comonomer conc. [mol/l]	1,5-HD- conc. [mol/l]	comon. conc. [mol/l]	1,5-HD molar ratio.	yield [g]	activity [gP./molTi* h*(mol/l)]	hexadiene- content [mol/% ^{e)}	T _m ^{f)} [°C]	T _g ^{f)} [°C]	M _n ^{e)} [kg/mol]	M _w /M _n ^{e)}
b) copolymerization with styrene											
6	styrene	1,7	0,4	1 : 4	0	0	0	-	-	-	-
7	styrene	1,1	1,1	1 : 1	0	0	0	-	-	-	-
8	styrene	0,4	1,7	4 : 1	h)	0	0	n.d.	n.d.	n.d.	n.d.
c) copolymerization with ethene (ethene pressure 1,5 bar)											
9	ethene	0,22	0,22	1 : 1	1,13	160	31,2	57	-6	5,1	2,1
10	ethene	0,42	0,22	1 : 2	0,86	192	40,0	-	3	6,4	6,0
11	ethene	0,84	0,22	1 : 4	1,37	174	47,7	-	16	8,0	9,3
12	ethene	1,68	0,22	1 : 8	2,64	181	52,4	-	25	i)	i)
d) terpolymerization with ethene and styrene (ethene pressure 2,5 bar)											
13	ethene/ styrene	0,22	E: 0,22	1 : 1 : 1	4,52 ^{d)}	13.688	HD: 19,3	70	-6	10,2	2,6
			S: 0,22				S: 2,1				
a) Polymerization conditions:											
	b)		[cat] = 100 μmol/l,	Al:Ti = 2000,	t = 8 h,	T = 20°C					
	c)		[cat] = 80 μmol/l,	Al:Ti = 2000,	t = 1 h,	T = 20°C,					
	d)		[cat] = 20 μmol/l,	Al:Ti = 2000,	t = 15 min,	T = 60°C					
e) by NMR-spectroscopy											
f) by differential scanning calorimetry (DSC)											
g) by gel permeation chromatography (GPC)											
h) traces of polystyrene i) crosslinking in high-temperature GPC											

As apparent in Table 2 styrene did not copolymerize with 1,5-hexadiene. This is in accord with propene/styrene copolymerizations where the same catalytic system is inactive as well (13). In contrast to 1,5-hexadiene/styrene copolymerization, copolymerization of 1,5-hexadiene with ethene was possible. Catalytic activity was found independent of comonomer concentration. Copolymer molecular masses were low with $M_n = 8.000$ g/mol and molecular weight distributions varying between $M_w/M_n = 2$ and 9,3. This was surprising, because molecular weights of the homopolymers were much higher (Table 1). It seems that the copolymerization results in conformations of the growing chain at the metal centre that are especially favourable for agostic interactions, thus leading to β -hydrid-elimination. Interestingly, the hexadiene content of the copolymers is very high with already 31,2 mol-% incorporation for a 1:1-ratio in the monomer feed. Calculation of copolymerization parameters according to Kelen-Tüdös resulted in $r_E = 1,5$ and $r_{HD} = 0,2$ ($r_E \cdot r_{HD} = 0,3$), indicating blockiness of ethene incorporation.

With a content of less than 32 mol-% methylene-1,3-cyclopentane units copolymers became semicrystalline. The melting temperature for a copolymer with 31,2 mol-% cyclic units is 57°C. Glass transition temperatures (T_g) rapidly increased with increasing content of cyclic units, from $T_g = -6^\circ\text{C}$ to 25°C for copolymers corresponding to a content of cyclic units of 31,2 mol-% to 52,4 mol-%, respectively. Figure 1 shows the variation of T_g with the content of cyclic units in the copolymer.

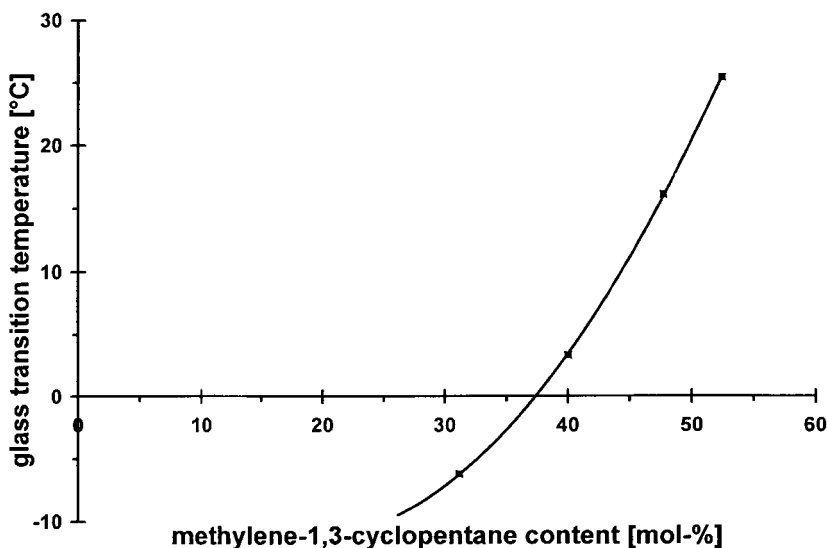


Figure 1 Glass transition temperature versus hexadiene content of copolymers

In the presense of ethene it was possible to obtain ethene/styrene/1,5-hexadiene terpolymer, although styrene/1,5-hexadiene copolymerization had failed. According to run 13 (Table 2), the terpolymer contented 2,1 mol-% styrene and 19,3 mol-% hexadiene. A monomer ratio of 1:1:1 in the monomer feed resulted in a much higher incorporation of hexadiene than styrene. This is in good agreement with the results of ethene/hexadiene copolymerization shown above and those of ethene/styrene copolymerization reported in a

previous publication (12). With a melting temperature of 70°C and a melting enthalpy of 22 J/g this terpolymer was semicrystalline. From run 9 and run 13 (Table 2) it is apparent that low styrene incorporation seems to have a high impact on thermal transitions of ethene/1,5-hexadiene copolymers. To our knowledge this is the first example of a random linear copolymer simultaneously incorporating both cyclic and styrenic units.

Figure 2 depicts the ^{13}C -NMR spectrum of the terpolymer poly(ethene-co-styrene-co-1,5-hexadiene). The small peak at 45,5ppm and the absence of a peaks at 41ppm (polystyrene) confirm the existens of isolated styrenic units in the chain and the absence of polystyrene or longer styrene blocks. Signals at 31,9ppm and 32,9ppm are identified as the methylene carbons of isolated cyclic units in cis- (c_i) and trans-rings (t_i) respectively. Signals at 32,2ppm and 33,4ppm correspond to the methylene carbons of cyclic units next to each other, again in cis- (c_s) and trans-configuration (t_s) respectively.

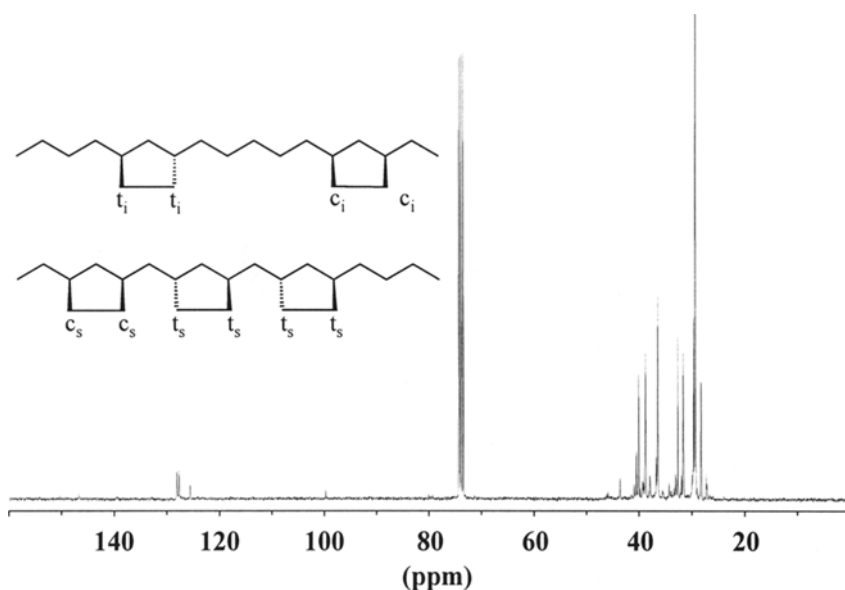


Figure 2 ^{13}C -NMR spectrum (75,4 Mhz, $\text{C}_2\text{D}_2\text{Cl}_4$, 100°C) of a terpolymer poly(ethene-co-styrene-co-1,5-hexadiene)

In conclusion, MAO-activated $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N-t.}-\text{butyl})\text{TiCl}_2$ gave homopolymers and random copolymers of 1,5-hexadiene with ethene with high hexadiene content and random distribution of cis- and trans-rings, where the ratio of methylene-1,3-cyclopentane rings to vinyl side chains was controlled by 1,5-hexadiene concentration. Obviously, high 1,5-hexadiene concentration adversely affects cyclopolymerization, thus producing vinyl side chains. Thermal transitions can be controlled by comonomer content. It was possible to produce cycloolefin copolymers with vinyl functionality as well as cycloolefin copolymers containing styrenic units.

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References

1. a) Kaminsky, W., Bark, A., Spiehl, R., Möller-Lindenhof, N., Nieboda, S. in *Proceedings, International Symposium on Transition Metals and Organometallics as Catalysts for Olefin Polymerization*, ed by Kaminsky, W., Sinn, H., Springer Press, Berlin 1988, p.291 b) Kasminsky, W., Spiehl, R., *Macromol. Chem. Phys.* (1989), **190**, 515
2. Herfert, N., Montag, P., Fink, G., *Macromol. Chem Phys.* (1993), **194**, 3167
3. Collins, S., Kelly, W. M., *Macromolecules* (1992), **25**, 233
4. Boor, J., "Ziegler-Natta-Catalysts&Polymerization", Academic Press, New York 1979, p. 526
5. Cherdron, H., Brekner, M.-J., Osan, F., *Angew. Makromol. Chem.* (1994), **223** 121
6. a) Resconi, L., Waymouth, R. M., *J. Am. Chem. Soc.* (1990), **112**, 4953 b) Coates, G. W., Waymouth, R. M., *J. Am. Chem. Soc.* (1991), **113**, 6270 c) Resconi, L., Coates, G. W., Mogstad, A., Waymouth, R. M., *J. Macromol. Sci. Chem. Ed.* (1991), **A28**, 1225 d) Coates, G. W., Waymouth, R. M., *J. Am. Chem. Soc.* (1993), **115**, 91
7. Jeremic, D., Wang, Q. Y., Quyoum, R., Baird, M. C., *J. Organomet-. Chem.* (1995), **497(1-2)**, 143
8. Schaverien, C. J., *J. Mol. Catal.* (1994), **90(1-2)**, 177
9. Cavallo, L., Guerra, G., Corradini, P., Resconi, L., Waymouth, R. M., *Macromolecules* (1993), **26(2)**, 260
10. Shapiro, P. J, Bunel, E., Schaefer, W. P., Bercaw, J. E., *Organometallics* (1990), **9**, 867
11. EP 0416815 A2 (1990), The Dow Chemical Company, invs.: Stevens, J. C., Timmers, F. J., Wilson, D. R., Schmidt, G. F., Nickias, P. N., Rosen, R. K., Knight, G. W., Lai, S.-Y.
12. Sernetz, F. G., Mülhaupt, R., Waymouth, R. M., *Macromol. Chem. Phys.* (1996), **197**, 1071
13. Sernetz, F. G., Mülhaupt, R., Waymouth, R. M., unpublished results