Nuclear Magnetic Resonance Evidence for a New Microstructure in Ethene–Cyclopentene Copolymers

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ABSTRACT: We have analyzed the microstructure of a series of copolymers of ethene and cyclopentene prepared with a novel ferrocene-substituted catalyst using one- and two-dimensional ^{13}C- and ^{1}H-NMR methods. Up to 64% of the cyclopentene is incorporated as 1,3-cyclopentylene units, which has not been observed previously in copolymers. The subspectra were derived based on a triad model. The polymers appeared to be *atactic* with mainly *cis*-incorporated cyclopentylene units. No ring opening could be detected.

Introduction

Copolymers of olefins with cycloolefins are of considerable interest because of their optical properties and high glass transition temperatures, which make them suitable as starting materials for optical disks and fibers. The macroscopic properties of these polymers are highly dependent on the microstructure. Analysis of the composition (relative amounts of cycloalkane units), tacticity, and diastereomerism can readily be obtained from NMR spectra of polymer solutions.[1–3] Under suitable conditions quantification is calibration independent, which makes NMR a unique tool for calibrating other (faster and cheaper) methods of quantitative analysis, such as IR spectroscopy.

The use of chiral zirconocenes as polymerization catalysts is well established for the copolymerization of olefins. Using catalytic complexes different from those in previous reports,[4,5] we prepared new copolymers of ethene and cyclopentene with unique microstructural features as described below.

Since the ^{13}C-NMR spectra of these polymers deviated from what has been published previously,[4] we report a thorough investigation of the NMR-spectroscopic properties and microstructural domains derived.

Since chemical shift prediction could not be used as a stand-alone approach to the assignment, one- and two-dimensional heteronuclear correlated NMR methods (i.e., HC-COSY and modified HHC-RELAY) were used.

Experimental Section

Polymerization. The polymerization catalyst used, *rac*-dimethylsilanediyl(ferroceno[2,3]inden-1-yl)(cyclopentadienyl)-zirconium dichloride (Figure 1) was prepared as described earlier.[6,7] A total of 50% of the required methylaluminoxane was placed in a 2-L reactor together with 500 mL of either pure cyclopentene or a mixture with *n*-hexane (Table 1) and stirred in a dry nitrogen atmosphere for 15 min. After the reaction temperature had settled, the reactor was filled with ethene and the catalyst solution (remaining methylaluminoxane and 10 mg of metallocene dissolved in 5 mL of toluene) was added through a pressure sluice. The ethene pressure was maintained at 1 bar for 2 h (if not stated otherwise), while constantly stirring at 700 rpm. The reaction conditions and relative amounts are summarized in Table 1. The polymers were filtered and stirred in 0.1 M NaOH to remove the residual catalyst.

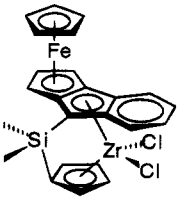

Figure 1. Catalyst: *rac*-dimethylsilandiyl(ferroceno[2,3]inden-1-yl)(cyclopentadienyl)zirconium dichloride.

NMR Measurements. NMR spectra were measured on a Bruker WM-360 retrofitted with digital phase shifters (360.13 MHz ^{1}H, 90.56 MHz ^{13}C). Chemical shifts were referenced to the solvent signals of tetrachloroethane ($\delta = 74.0$ for ^{13}C, $\delta = 7.00$ for ^{1}H). Heteronuclear correlation spectra were acquired using modified Bruker microprograms from the DISR89 software release (DEPT.AU, XHCORR.AU, RELAY2.AU). The modifications pertained to phase cycling to allow phase-sensitive acquisition (TPPI method) for the correlation experiments. In the relay experiment the second proton 90° pulse was substituted by a 60° pulse to compensate for evolution of large passive homonuclear coupling constants.[8,9]

The sample solutions, 10 wt % in trichlorobenzene/benzene-d_6 (3:1) for 1D ^{13}C spectra of in tetrachloroethane-d_2 for heteronuclear correlation spectra, were prepared by sonification at 400 K for 4 h and measured at 370 K.

For quantitative analysis spectra were acquired using 90° (8.6 μs) excitation pulses with power-gated composite pulse decoupling (WALTZ). The repetition delay of 13.5 s was determined such that a further increase by 50% did not change the integral ratios of the two largest integrals by more than 2%. The digital resolution before zero filling was 0.649 Hz/Pt (0.325 Hz/Pt after zero filling to 64 K). Shorter repetition delays (2.2 s) were used when no quantification was required. The integration limits are summarized in Table 2. Only ^{13}C signals of the same multiplicity (CH_2) were used for the quantification.

Results and Discussion

The main features of the ^{13}C-NMR spectra can be seen in the spectrum of sample 7 (Figure 2), which contains 22.3 mol % of cyclopentene monomer units. By comparison with the spectrum published in ref 4, it is immediately clear that additional signals are present in our sample. Assignments of these signals were

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Table 1. Sample Number, Ratio Methylaluminoxane/Metallocene (Al/Zr), Vol % Cyclopentene in *n*-Hexane, Ethylene Pressure, Cyclopentylene Content, 1,3/1,2 Incorporation Ratio, Mean Molecular Weight, and Melting Point

sample no.	temp (°C)	Al/Zr	vol % Cp	Et pressure (bar)	% Cp	1,3/1,2	$M_w \times 10^3$	T_m (°C), under N_2
1	50	5000	100	1	1.8	0.17	37	121
2	50	1000	100	1	1.9	0.19	32	122
3	70	2250	50	1	2.9	1.15	16	123
4	50	2250	100	1	3.0	0.45	29	118
5	70	2250	80	1	9.8	1.06	7	110
6	70	2250	100	0.5	16.2	1.75	12	105
7	70	2250	100	1	22.3	1.75	3	105
8	70	2250	100	0	100	2.50	<10	T_g

Table 2. Complete Peak Assignment and Integration Limits[a]

integral limits	shift range	multiplicity	sequence	atom
I1	23.06	S	*eoe*	4
	24.32	S	*coc*	4
	25.57	S	*coe*	4
	25.76	S	*ccocc*	4
	28.20–29.31	S	*cee*	*b*
	30.04–30.38	S	*ceeee*	*g*
I2	30.04	S	*eeeee*	
	30.90	S	*ccmcc*	4,5
	30.98	S	*eoe*	3,5
	31.80–32.00	S	*cme*	4
	31.80–32.50	S	*ccocc*	3,5
	32.00–33.30	S	*cme*	5
I3	32.12	S	*eme*	4,5
	32.24	S	*coe*	3
	32.70–33.30	S	*cmc*	4,5
	33.10	S	*coe*	5
	33.27	S	*coc*	3,5
I4	34.60–36.00	S	*cec*	*a*
	36.00–37.10	S	*cee*	*a*
I5	37.70–39.04	S	*ccmcc*	2
	39.20–41.10	S	*cme*	2
	39.20–41.10	S	*cmc*	2
	39.25	T	*cme*	3
	40.60	T	*coe*	2
	40.65	T	*eme*	1,3
	41.10	S	*eme*	2
	43.16	T	*eoe*	1,2
	46.00–47.00	T	*cmc*	1,3
	46.08–46.30	T	*coe*	1
	46.43	T	*coc*	1,2
	46.70–47.20	T	*ccocc*	1,2
	46.70–47.20	T	*ccmcc*	1,3
	47.00	T	*cme*	1

[a] If no shift range is given, the signal appears in an interval of up to ±0.05 ppm. The multiplicity is termed S for secondary and T for tertiary carbons. I1 to I5 represent the integrals in the corresponding intervals. The cyclopentylene content was calculated as $[2(I1 + I5) + I3]/(I2 + I3 + I4)$.

obtained by heteronuclear correlation experiments and chemical shift calculations[10,11] based on the triad model described below.

The key to interpretation is the assumption of 1,3-disubstituted cyclopentane units in addition to the expected 1,2-disubstituted units, which were found exclusively in the previously published work on cyclopentene copolymers.[4] Recently 1,3-cyclopentylene units have been shown to exist in pure polycyclopentene.[12] The existence of both, 1,2- and 1,3-cyclopentylene building blocks increases the number of possible triads in the copolymer to $3^3 = 27$ (excluding stereoisomerism). Therefore, a convenient shorthand notation for the monomeric units and carbon resonances is used:

The character *c* represents a general cyclopentylene unit. Further distinction is made by the letters *o* (*ortho*) to specify 1,2-disubstituted and *m* (*meta*) to specify 1,3-disubstituted rings. The ethylene units are designated *e*. Three or five of these characters represent a triad or a pentad sequence, where the central character designates the entity to which the signals belong. The cyclopentylene carbons are numbered as shown in Figure 3. The ethylene carbons are termed α, β, γ, ... according to their distance from the nearest tertiary carbon.

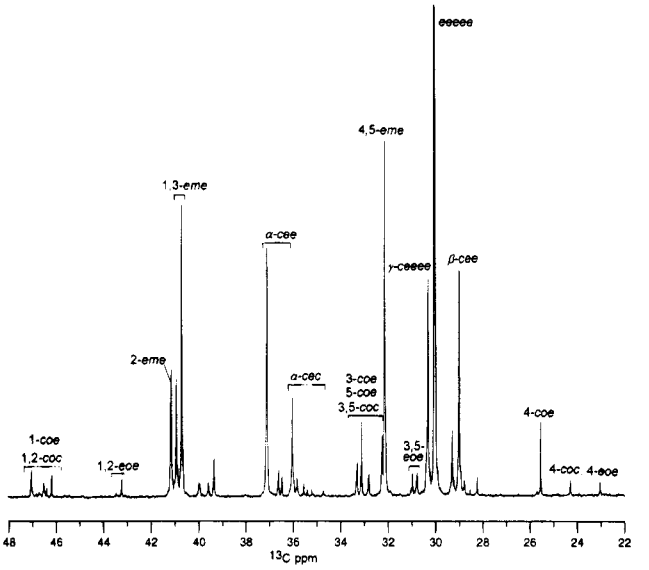

Figure 2. ^{13}C spectrum of sample 7 (22.3 mol % cyclopentylene) with the assignment of important signals (see text for an explanation of the nomenclature used for peak labeling).

Figure 3 shows the complete set of all triads and pentads (excluding steroisomerism) we derived from the spectra of the copolymer samples investigated together with the corresponding stick spectra. The sequences can be classified into symmetric and asymmetric ones with respect to the central monomeric unit. The symmetric sequences centered around cyclopentylene (*eoe*, *coc*, *ccocc*, *eme*, *cmc*, *ccmcc*) give rise to three signals with the amplitude ratios 1:2:2, whereas asymmetric sequences (*coe*, *cme*) exhibit five signals of equal integral. Exploiting this property permitted a thorough peak assignment. The schematic spectra in Figure 3 are drawn in a DEPT-like manner (that is, signals from tertiary carbons appear negative). The complete peak assignment is summarized in Table 2. Combinations of these stick spectra can be used to simulate experimental spectra in a synthetic approach similar to the one in ref 1.

The assignments of ring carbon signals were confirmed by correlation to adjacent carbon atoms by an optimized HHC-RELAY experiment (a shorter homonuclear transfer delay, 15 ms, because of the fast transverse relaxation and a 60° proton pulse as described in the Experimental Section were used). The HHC-RELAY spectrum of sample 7 (22.3% cyclopentylene) is shown in Figure 4. The relay peaks (2H → 1,3H → 1,3C(*eme*); 4,5H → 1,3H → 1,3C(*eme*); ...) in the spectrum are diagnostic of the indicated polarization transfer pathways. They corroborate the connectivities

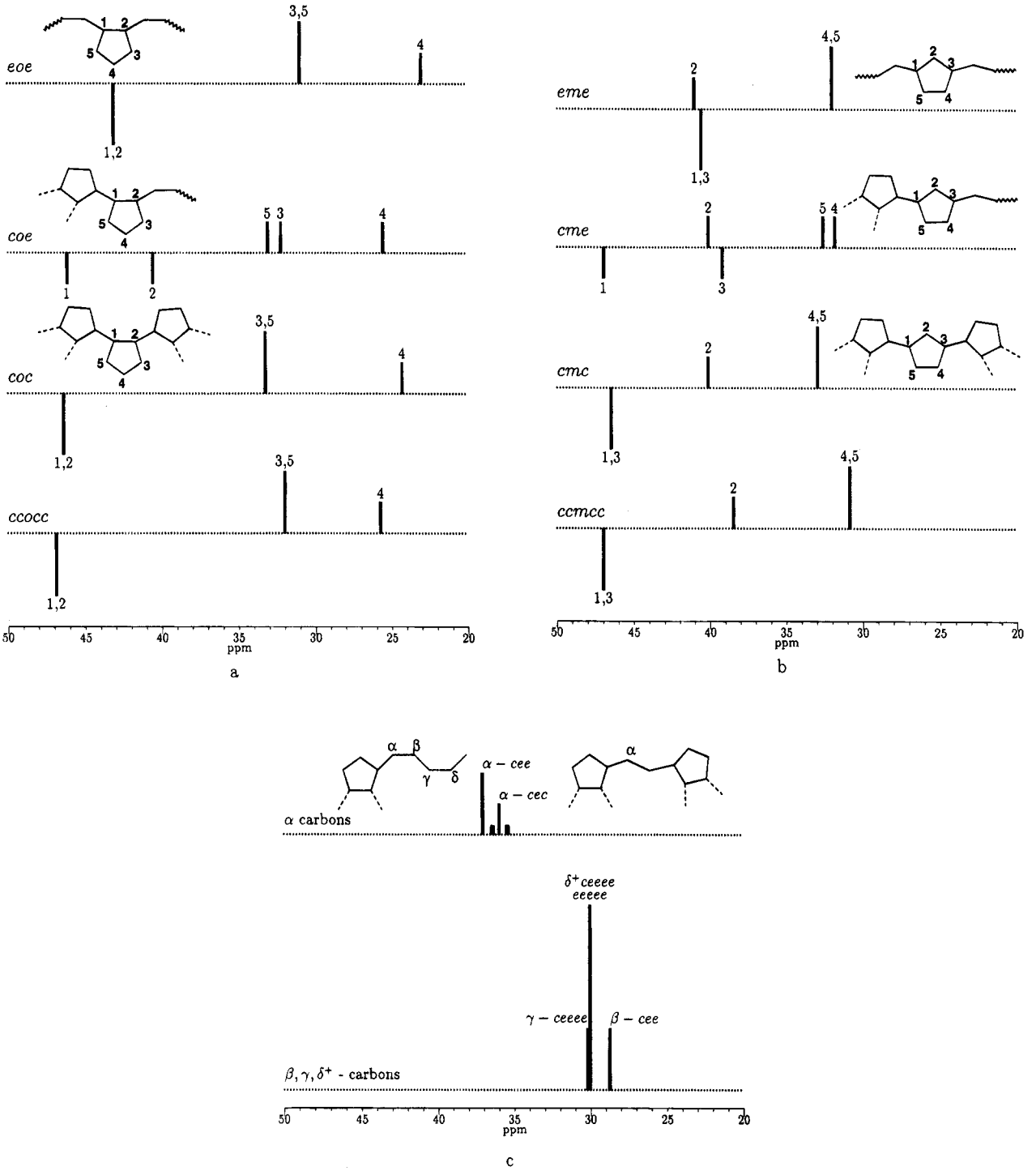

Figure 3. Complete set of all triad and pentad sequences used and their stick spectra. (The spectra are drawn in a DEPT-like manner; that is, methine signals appear negative.) Dashed bonds indicate that a ring substituent can be either 1,2- or 1,3-incorporated.

of the carbon atoms. Actually, they give final proof of the existence of 1,3-cyclopentylene units in the copolymers.

The assignment was further supported by comparison with the results from a chemical shift prediction program[11] and CSEARCH,[10] which uses a ^{13}C NMR data base. Excellent agreement was found for all ethylene sequences (*eeeee*, α,β,γ-*cee*, α-*cec*), whereas the chemical shifts of ring carbons deviated from the predictions (which, actually, can be explained by considering that the solvent and the high temperature cause additional shifts which cannot be predicted well enough). The signal assignments for the *eoe* sequence are in accordance with previously published ^{13}C NMR spectra by Kaminsky et al.[4] The chemical shift ranges of the *cme* and *cmc* carbons overlap as can be seen in Table 2. For quantitative evaluation therefore only integral values representing the sum of these triads were used. Quantitative analysis of the spectra served primarily to determine the cyclopentylene content in the polymers.

These data can also be used to derive the ratio of 1,3- over and 1,2-cyclopentylene incorporation (using integrals of the signals assigned to 4-*eoe*, 4-*coe*, 4-*coc*, 4-*ccocc*, 2-*eme*, 2-*cme*, 2-*cmc*, 2-*ccmcc*). There seems to be a positive correlation of this ratio to the total content of cyclopentylene units, as can be seen in Figure 5. The

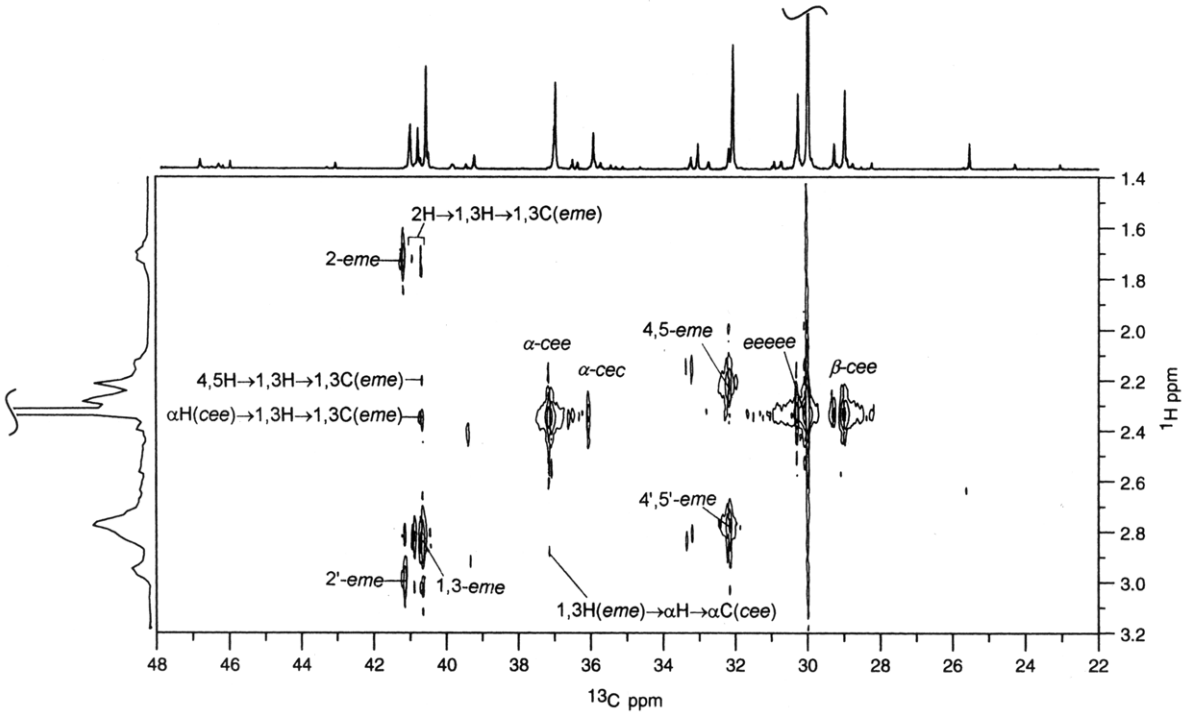

Figure 4. HHC-RELAY spectrum of sample 7. The assignments according to the described nomenclature (the numbers 2,2′,4,4′,5,5′, etc., refer to those in Figure 6), as well as the relay transfer pathways, are given for the key signals. In both dimensions one-dimensional spectra are given in place of projections. The proton spectrum has been resolution enhanced and is truncated at 13% of the highest signal, while the carbon spectrum is truncated at 43% of the highest signal.

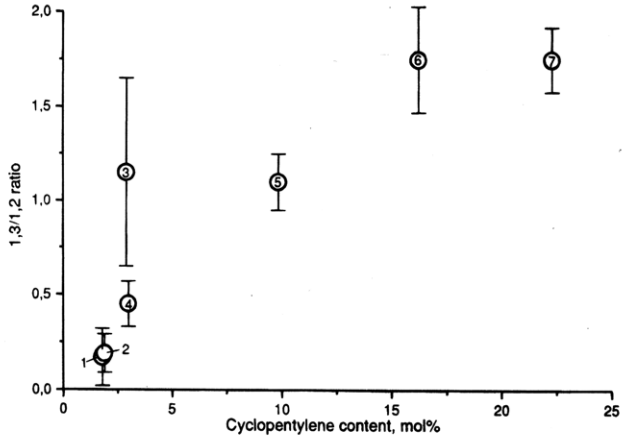

Figure 5. Plot: 1,3/1,2 ratio versus cyclopentylene content for the samples 1−7 with calculated error (see text).

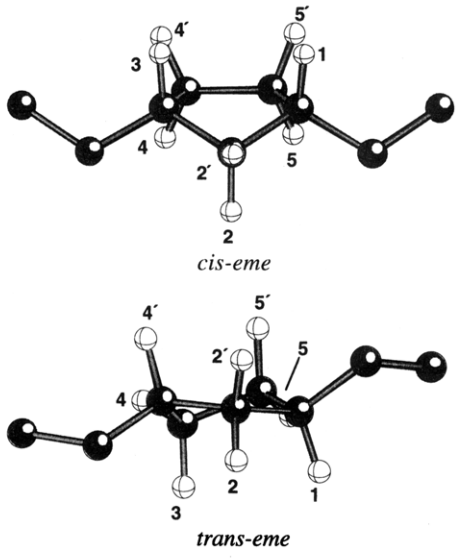

Figure 6. Local symmetry for 1,3-*cis* and 1,3-*trans-eme* structures generated by energy minimization (MMX) with PCMODEL[13] and drawn by Ball & Stick.[15]

error bars in Figure 5 represent a crude estimate of the measurement error: An absolute error of 50% of the weakest integral or signal intensity used for the calculation was assumed. The error remains acceptable for the 1,3/1,2 ratio. It is as small as ±0.2 mol % in the determination of the cyclopentylene content so that we refrained from giving these error bars. Thus, this method seems to be very stable with respect to the determination of the cyclopentylene content.

The degree of blocking was estimated for two samples which contained significant amounts of longer cyclopentylene blocks: sample 5 (14%) and sample 6 (61%). This number represents the ratio *ccccc*/(*ccccc* + *ece*).

Information about stereoisomerism can also be derived from the heteronuclear correlation experiments. The signals 2,2′,4,4′,5,5′-*eme* in Figure 4 belong to the geminal ring protons of the *eme* sequence of sample 7. These geminal protons have large chemical shift differences of up to 1.3 ppm, which can be interpreted as an indication of *cis*-incorporation of 1,3-cyclopentylene on the following grounds. As *trans*-1,3-cyclopentylene units exhibit local C_2 symmetry, the geminal 2-*eme* protons should have very similar chemical shifts, while a large difference in the local environment exists for *cis*-1,3-cyclopentylene, as can be seen from Figure 6, where structures derived from force-field calculations (MMX[13]) are shown. Only in one sample (7) could we see a significant fraction of *trans-eme* units characterized by a ^{13}C signal at 39.28 ppm. This assignment was based on spectra of pure polycyclopentene and ref 12. For blocked structural domains like *ccmcc*, both *cis*- and *trans*-incorporation were found using a *J*-filtered HHC-RELAY spectrum.[14] The *cis*/*trans* ratio was quantified

for cyclopentylene blocks: 10.0% of *ccmcc* sequences and 2.9% of *ccocc* sequences are *trans* in sample 8, which is pure polycyclopentene.

From the variation of polymerization conditions (Table 1) we could not see a significant influence of the relative amount of aluminoxane. However, increased temperature and higher cyclopentene concentrations favor, as expected, the cyclopentene incorporation. Moreover, they increase the formation of 1,3-cyclopentylene units. There seems also to be a dependency of the 1,3/1,2 ratio on the mean molecular weight. Investigations in progress indicate that using a sterically more demanding ligand on the zirconium catalyst suppresses isomerization of the cyclopentane units, leading to a higher 1,2-cyclopentylene content.

Conclusions

Mechanistically the formation of 1,3-cyclopentylene units can be explained by isomerization of the primary addition product formed from the cyclopentene–catalyst complex. This is corroborated by the finding that the ratio of 1,3 over 1,2 units increases with the cyclopentylene content of the copolymer. Since at higher concentrations of cyclopentene during the polymerization process a larger fraction of cyclopentene is bound to the catalyst, there is also a higher likelihood for isomerization. Further catalysts are under investigation with respect to their influence on the 1,3/1,2-cyclopentylene ratio, which is a new parameter with potential influence on material properties.

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