Unique microstructure analysis of ethylene-propylene copolymer synthesized using catalytic system based on α-diimine nickel complexes: A comparative study by 13C NMR technique

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ORIGINAL PAPER

Unique microstructure analysis of ethylene-propylene copolymer synthesized using catalytic system based on α-diimine nickel complexes: a comparative study by ^{13}C NMR technique

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Abstract The microstructure of rubber-like ethylene-propylene copolymer (**MN4**) produced by a mixed nickel-based system (**MN**) containing catalysts of dibromo[*N,N′*-bis(2,6-diisopropylphenyl)-2,3-butanediimine]nickel(II) **n1** and dibromo[*N,N′*-(phenanthrene-9,10-diylidene)bis(2,6-diisopropylaniline)]nickel(II) **n2** was determined by ^{13}C NMR technique. Sequences distribution of ethylene (E), propylene (P), EP, inverted propylene and uninterrupted methylene and also methylene number-average sequence lengths for the copolymer (**MN4**) were estimated. The results obtained from the **MN4** EP copolymer were compared with reported copolymers which had been synthesized using constrained geometry catalyst (CGC) and vanadium-based Ziegler-Natta catalyst. The results demonstrated that the **MN4** EP copolymer had fewer alternating comonomer sequences than ethylene-propylene elastomers obtained by CGC and vanadium-based (V) catalysts. A large number of the inversion structures (66 %) and high mole percent of sequences containing a long branch (3.2 mol%) were also observed in unique microstructure of the copolymer (**MN4**).

Keywords Nickel-based catalyst · Ethylene-propylene copolymer · Elastomers · Microstructure · NMR

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Introduction

Ethylene-propylene elastomers (EPM) are amorphous materials with a glass transition temperature of −50 to −60 °C and represent an interesting class of synthetic elastomers. The commercial EPM copolymers are generally made using homogeneous specific vanadium-based and heterogeneous isospecific titanium-based Ziegler-Natta catalysts. Single site metallocene catalysts based on zirconium and titanium activated with Methylaluminoxane (MAO) are used to produce EPM, too [1–5].

In 1995, Brookhart and coworkers synthesized a new class of polymerization catalysts based on Ni(II) and Pd(II) stabilized by bulky α-diimine ligands. The α-diimine complexes based on nickel(II) activated by MAO are able to polymerize α-olefins to form high molecular weight polymers and are also used in copolymerization of ethylene and propylene. The α-diimine nickel and palladium catalysts produce poly(α-olefin)s with very different structural properties from those obtained with conventional Ziegler-Natta or metallocene catalysts. The bulky substituent on the aryl group of the diimine ligand blocks associative olefin exchange and β-hydride elimination to produce the polymer with high molecular weight. Control over the catalyst structures, cocatalyst, and polymerization conditions allows one to readily produce a variety of materials, ranging from highly viscous liquids and highly branched to rigid linear polyethylene by adjusting the competition between chain walking and chain propagation processes [6–13].

Extensive research has been carried out to relate the physical properties and performance of EPM samples with their chain structure. Among different methods for the structural characterization, ^{13}C NMR has been found to be the most effective technique. Carman and coworkers carried out a comprehensive analysis, treating EPM as a terpolymer with ethylene, normal (head-to-tail) propylene and inverted propylene as the termonomers. In Cheng's paper, efforts were made to use high-field ^{13}C NMR to review the assignments of the spectrum of EPM. Using Cheng's assignments, has been obtained more accurate information on copolymer composition, sequence distribution, and tacticity [2, 14–16].

In this work, microstructure of rubber-like ethylene-propylene copolymer obtained by α-diimine nickel catalysts was determined by ^{13}C NMR technique. The α-diimine nickel catalysts had been used because of their specific behavior (β-hydride elimination and chain walking reactions) for ethylene-propylene copolymerization to produce different copolymer than those obtained by conventional catalysts. The α-diimine catalysts were bearing bulky substituent (isopropyl) in *ortho* aryl positions of the ligand. The comonomer sequences distribution, uninterrupted methylene sequences distribution and methylene number-average sequence lengths for the copolymer were estimated. A comparison with reported copolymers which had been synthesized using CGC and vanadium-based catalysts is also presented in this paper.

Experimental section

Materials, instruments and polymer characterization

Methanol was supplied by Merck Chemical Co. (Darmstadt, Germany) and was used without any purification. Toluene was obtained from Arak Petrochemical Co. (Arak, Iran), it was dried by refluxing over sodium wire/benzophenone and then distilled under dry N_2 and stored over activated 4 Å/13X type molecular sieves. Toluene was used as solvent of the catalyst slurry and polymerization medium. Methylaluminoxane (MAO) was purchased from Sigma Aldrich Chemicals (Steinheim, Germany) as 10 wt% (1.5 M) solution in toluene. Polymer grade ethylene and propylene were obtained from Arak Petrochemical Co. (Arak, Iran) and it was used after passing through a column of activated 4 Å/13X type molecular sieves. Nitrogen was obtained from Roham Gas (Tehran, Iran) dried by passage through KOH, activated silica gel and 4 Å/13X type molecular sieve columns.

Synthesis of the catalysts **n1** and **n2** have been described in detail in our previous work (see Fig. 1) [17].

Dry toluene (200 mL) and MAO solution (10 wt% in toluene) were used as solvent and cocatalysts respectively. A mixed of 1:1 w/w of the nickel-based catalysts **n1** and **n2** (3.0×10^{-3} mmol) (**MN**) was suspended in toluene and was transferred into a stainless steel Buchi AG reactor (CH-8610) under nitrogen. Monomer injection system was equipped with mass flow controller (MFC) that loading of reactor was accomplished with the flow control of mixed of ethylene and propylene gasses in a fixed ratio. Toluene was saturated with a constant ratio from mixture of the both gases prior to the polymerization. After the desired reaction time, copolymerization ended with transfer of the reaction mixture into methanol containing HCl (5 %). The reaction mixture was stirred for 30 min, filtered and the polymer was washed with methanol and water several times and was dried for 12 h at 40 °C.

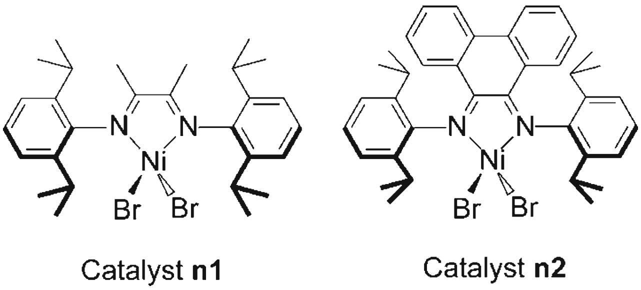


Fig. 1 Structures of nickel diimine complexes: dibromo[*N,N′*-bis(2,6-diisopropylphenyl)-2,3-butanediimine]nickel(II) **n1** and dibromo[*N,N′*-(phenanthrene-9,10-diylidene)bis(2,6-diisopropylaniline)]nickel(II) **n2**

Direct application of Mark-Houwink equation of the form $[\eta]=3.8\times10^{-4} M_v^{0.74}$dL g^{-1}, displayed the so-called viscosity average molecular weight, M_v [18]. The M_v of the copolymer samples were measured in decaline (decahydronaphthalene) at 135±1 °C by means of Ubbelohde suspended level dilution viscometer. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch 200 F3 DSC instrument under an N_2 atmosphere. The samples were heated from −100 to +200 °C with a rate of 10 °C min^{-1}. The glass transition temperature (T_g) of the copolymers were determined by DSC. The molar proportion of ethylene and propylene units in the copolymers were determined using an IR method (Shimadzu FTIR-4300) [19]. ^{13}C NMR technique was utilized to determine the microstructure of the ethylene-propylene copolymer. The 100.6 MHz ^{13}C NMR spectrum was recorded on a Bruker Avance 400 spectrometer with broad-band proton decoupling at 120 °C and used a 90° pulse with a relaxation delay of 4 s. The sample solution was prepared in 1,2,4-trichlorobenzene at a concentration of around 10 wt%. The chemical shifts were referenced internally to the major backbone methylene carbon resonance, which was taken as 30.00 ppm. The main assignments and calculations were used to estimate the comonomer sequence distribution and methylene sequence length according to literature [2–4, 14, 20].

Result and discussion

Table 1 shows the catalytic activity behavior, M_v, ethylene content and T_g of obtained copolymers when Al/Ni molar ratio, propylene/ethylene relative pressure (P_{Pr}/P_{Et}) and temperature were varied from 1,000:1 to 3,000:1, 1:1 to 9:1 and 20 to 60 °C, respectively. The activity of catalysts **n1** and **n2** in the copolymerization of ethylene with propylene were 920 and 1,280 (g copolym/mmol Ni.h), respectively (runs **10** and

Table 1 Influence of MAO concentration, temperature and monomer relative pressure on copolymerization of ethylene-propylene using catalytic systems (**n1**, **n2** and **MN**)

Run	Copolymerization conditions				Results				
	n1/**n2** (w/w)	[Al]/[Ni]	P_{Pr}/P_{Et}	Temp.(°C)	Yield (g)	Activity[a]	T_g (°C)	Et (%)	M_v (g/mol)
1	1:1	2,000:1	1:1	20	3.825	2,550	−57.0	72.2	3.89×10^5
2	1:1	2,000:1	3:1	20	2.482	1,655	−56.2	64.4	3.72×10^5
3	1:1	1,000:1	5:1	20	1.140	760	–	58.1	1.97×10^5
4	1:1	2,000:1	5:1	20	1.620	1,080	−54.3	59.0	2.22×10^5
5	1:1	3,000:1	5:1	20	1.608	1,072	–	61.8	2.53×10^5
6	1:1	2,000:1	7:1	20	1.342	895	−45.5	56.0	2.02×10^5
7	1:1	2,000:1	9:1	20	0.732	488	−32.3	51.5	1.36×10^5
8	1:1	2,000:1	5:1	40	0.700	467	–	63.5	1.52×10^5
9	1:1	2,000:1	5:1	60	0.240	160	–	69.5	1.18×10^5
10	1:0	2,000:1	5:1	20	1.380	920	–	63.7	2.11×10^5
11	0:1	2,000:1	5:1	20	1.920	1,280	–	57.1	2.43×10^5

Copolymerization conditions: $[Ni]=1.5\times10^{-5}$ M, $P_t=5$ bar, reaction time=30 min, toluene=200 ml. Results obtained from reference 17

[a] Activity in (g EPM/mmol Ni.h)

11, Table 1). The activity of the catalyst **n2** was higher than the catalyst **n1**. The behavior could be due to less electron density around the nickel metal center which increased activity of the catalyst **n2** [17, 21]. The M_v of the copolymers produced using catalysts **n1** and **n2** were 211,000 and 243,000 (g/mol), respectively. The catalyst **n2** produced a polymer with different M_v compared to the catalyst **n1**. Copolymerization using mixed catalysts **n1** and **n2** led to form several catalytic active centers with different behavior which applying this catalytic system has contributed to produce a large range of molecular weight. The best elastomeric figure were observed at the P_{Pr}/P_{Et} about 5:1, Al/Ni molar ratio about 2,000:1 and temperature of 20 °C (runs **4**, **10** and **11**, Table 1). Various runs of the copolymerization using the catalysts **n1**, **n2** and mixed of 1:1 of them (**MN**) have been described in detail in our previous work [17]. The most rubber-like copolymer (**MN4**) was colorless and the ethylene content, M_v and T_g of the copolymer were 59 %, 222,000 g/mol and −54.3 °C (run **4**, Table 1), respectively.

Microstructure of the ethylene-propylene copolymer

The ^{13}C NMR spectrum of the rubber-like copolymer (**MN4**) produced using the nickel-based α-diimine catalyst system (**MN**) is shown in Fig. 2.

Four types of nomenclature to determine the complete microstructure of the copolymer (**MN4**) are shown in Table 2. In the third column of the Table 2, the nomenclature of Cheng [14] and Galland et al. [20] was used where the position of the types of carbons and tacticity around each carbon have been determined. In the nomenclature, *m* and *r* refer to the meso and racemic which are defined for tacticity of paired branches, respectively (see **f** in Scheme 1) [14]. Also, sequences of ethylene unit (E) [CH_2–CH_2], propylene unit (P) [CH_2–$CH(CH_3)$], inverted propylene unit (P*) [$CH(CH_3)$–CH_2], α-olefin unit with a long branch (L) [CH_2–$CH(CH_2)_nCH_3$], unit containing a 2-methyl hexyl branch (2MH) [CH_2–$CH(CH_2)_4CH(CH_3)_2$], unit containing an *i*-butyl branch (*i*Bu) [CH_2–$CHCH_2CH(CH_3)_2$] have been determined. In the fourth column, the nomenclature of Usami and Takayama [22] was used. xB_n shows the presence of carbon x in the branch with length n (for branches starting with the methyl as "1" and for the backbone carbons as Greek letters and "br") (see **g** in Scheme 1) [23].

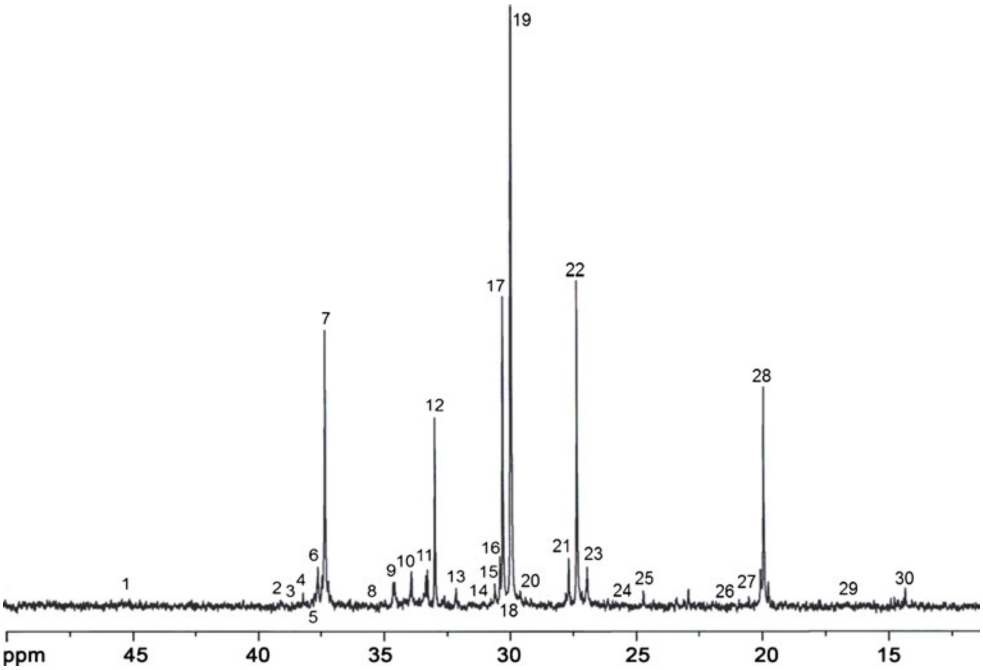
In the fifth column of Table 2, the nomenclature of Carman and coworkers [15] was used. The position of each of methyl (P), methylene (S) and methine (T) carbons relative to their nearest methine groups has been labeled by two Greek subscripts (see **a**, **b**, **c**, and **d** in Scheme 1) [14]. The first and second columns of Table 2 show the peak number and chemical shift related to types of carbons and their sequences.

Equations (1)–(24) are used for quantitative analysis of the copolymer (**MN4**) [2, 20]. The resonance integrals, I_x, where x is the peak number, are related to the various detected structures and are shown with their triad sequences. The quantitative analysis results obtained from Eqs. (1)–(15) are exhibited in Table 3.

In the following Equations, k is the normalization constant.

$$[\mathrm{EEE}] = k(I_{19}/2) \tag{1}$$

Fig. 2 ^{13}C NMR spectrum of the ethylene-propylene copolymer (**MN4**) synthesized by the catalytic system (**MN**)



$$[\mathrm{PEE}+\mathrm{EEP}]=k(I_{23}-3I_{13}-3I_2-2I_{24}) \tag{2}$$

$$[\mathrm{EPE}]=kI_{12} \tag{3}$$

$$[\mathrm{PEP}]=kI_{25} \tag{4}$$

$$[\mathrm{PPE}+\mathrm{EPP}]=k(I_{17}+I_{18}-(I_8+I_{10}/2)-3I_{13}-2I_2-2I_{24}) \tag{5}$$

$$[\mathrm{PPP}]=k(I_{21}-I_2) \tag{6}$$

$$\left[\mathrm{PP^*P}\right]=k(I_5-I_{13}-I_2) \tag{7}$$

$$\left[\mathrm{PPP^*}\right]=kI_{29} \tag{8}$$

$$\left[\mathrm{PP^*PP}\right]=kI_8 \tag{9}$$

$$\left[\mathrm{P^*P^*PP}\right]=k(I_{10}/2) \tag{10}$$

$$1,4\text{-}\mathrm{B}_1 \ \text{ between } \ \mathrm{Ethylene}=k(I_{11}/2) \tag{11}$$

$$1,6\text{-}\beta\ \mathrm{B}_1=k(I_{22}-I_2)/2 \tag{12}$$

$$[\mathrm{ELE}]=kI_{13} \tag{13}$$

$$[\mathrm{E}i\mathrm{BuE}]=kI_{24} \tag{14}$$

$$[\mathrm{E2MHE}]=kI_2 \tag{15}$$

The presented triad sequences in Table 3, such as [EPE], [PEP] and [PPE + EPP] were obtained about 17.2, 4.6 and 2.1 mol% in the copolymer (**MN4**), respectively. All the obtained values in Table 3 show the copolymer composition produced by the catalytic system (**MN**).

The structures of metallocene EPM samples were without significant structures of tail to tail and head to head. However, EPM synthesized using vanadium-based catalysts contained a large number of inverted propylene units. Presence of inverted propylene sequences in the copolymer structure changes the number of consecutive methylene units. Hence, the inverted propylene units can form the structures of tail to tail and head to head with carbons $S_{\alpha\beta}$, $T_{\gamma\gamma}$, $T_{\gamma\delta}$ and $S_{\beta\gamma}$ (see **c**, **d**, and **e** in Scheme 1) [2, 14, 20, 24].

The **MN4** EPM copolymer contained structures composed of inverted propylene sequences that could indicate the presence of sequences of [PPP*], [PP*PP], [P*P*PP] and 1,4-B_1 between ethylene with values of 3.1, 2.4, 3.7 and 4.0 mol%, respectively. In the unique structure of the copolymer,

Table 2 ^{13}C NMR Assignment of ethylene-propylene copolymer (**MN4**)

Peak number	Chemical shift experiment (ppm)	Sequence[a]	Sequence[b]	Carbon type[c]
1	46.28–44.28	$S_{\alpha\alpha}$		$S_{\alpha\alpha}$
2	39.20	E2MHE	$3B_{2MH}$	
3	38.71	r–$S_{\alpha\gamma}$		$S_{\alpha\gamma}$
4	38.30	r–$S_{\alpha\delta}$		$S_{\alpha\delta}$
5	37.98	PP*P	1,2-brB_1	$T_{\alpha\gamma}$
		ELE+E2MHE		
6	37.68	(m + other)–$S_{\alpha\gamma}$		$S_{\alpha\gamma}$
7	37.40	(m + other)–$S_{\alpha\delta}$		$S_{\alpha\delta}$
8	35.77–35.28	r–$S_{\alpha\beta}$		$S_{\alpha\beta}$
		PP*PP	1,4-$\acute{\alpha}$ B_1	$S_{\gamma\alpha\beta\delta}$
9	34.77–34.34	EP* PE + EP *PE	1,4-$\acute{\alpha}$ B_1(between E)	$S_{\delta\alpha\beta\delta}$
		E*i*BuE	α B_{iBu}	
		E2MHE	α B_{2MH}+$6B_{2MH}$	
		ELE	α $B_{6-n}+n$ B_{6-n}	
10	33.99	P*P*PP + P*P*PP	1,4-$\acute{\alpha}$ B_1	$S_{\gamma\alpha\beta\delta}$
11	33.67–33.28	EP* PE + EP *PE	1,4-brB_1(between E)	$T_{\gamma\gamma}$
				$T_{\gamma\delta}$
12	33.05	EPE	brB_1	$T_{\delta\delta}$
13	32.22	ELE	$3B_{6-n}$	
14	31.13	$T_{\beta\gamma}$ (m)+$T_{\beta\gamma}$ (r)		$T_{\beta\gamma}$
15	30.67	$T_{\beta\delta}$ (r)		$T_{\beta\delta}$
16	30.46	$S_{\gamma\gamma}$+$T_{\beta\gamma}$ (r)		$S_{\gamma\gamma}$
17	30.34	$T_{\beta\delta}$ (r)		$T_{\beta\delta}$
18	30.23	EEEP	γ B_1	$S_{\gamma\delta}$
19	30.00	EEE	δ B_1, δ B_{6-n}	$S_{\delta\delta}$
20	29.48	ELE	$4B_{6-n}$	
21	27.73	$T_{\beta\beta}$ (mm) + $T_{\beta\beta}$ (mr + rr)		$T_{\beta\beta}$
		PPP	brB_1	$T_{\beta\beta}$
		E2MHE	$4B_{2MH}$	
22	27.39		1,6-β' B_1	$S_{\beta\gamma}$
23	26.99	PEE + EEP	β' B_1	$S_{\beta\delta}$
		E*i*BuE	β B_{iBu}	
		ELE	β $B_{6-n}+(n-1)B_{6-n}$	
		E2MHE	$4B_{2MH}$	
24	25.46	E*i*BuE	$2B_{iBu}$	
25	24.95–24.27	PEP	β' B_1	$S_{\beta\beta}$
26	21.57–21.08	$P_{\beta\beta}$ (mm)		$P_{\beta\beta}$
27	21.08–20.37	$P_{\beta\beta}$ (mr)+$P_{\beta\gamma}$ (m)+$P_{\beta\delta}$ (m)		$P_{\beta\gamma}$
28	20.43–19.28	$P_{\beta\beta}$ (rr)+$P_{\beta\gamma}$ (r)+$P_{\beta\delta}$ (r)+$P_{\gamma\gamma}$		$P_{\gamma\gamma}$
29	17.09	PPP*	$1B_1$	$P_{\alpha\beta}$
	16.77			
30	15.00–14.00	PP*P	$1B_1$	$P_{\alpha\gamma}$
		ELE		

Referenced to isolated methylenes at 30.0 ppm

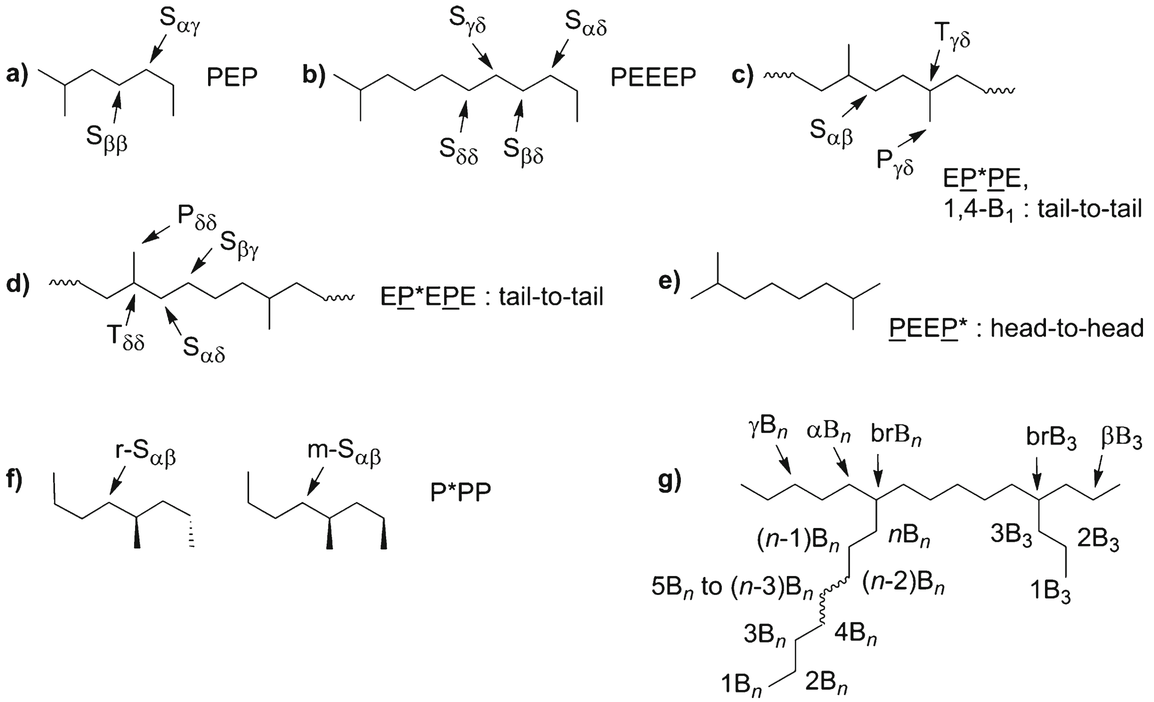
[a] From the nomenclature of Cheng [14] and Galland et al. [20] has been used

[b] From the nomenclature of Usami and Takayama [22] has been used

[c] From the nomenclature of Carman and coworkers [15] has been used

sequence of [ELE] and structure of 1,6-β' B_1 were about 3.2 and 11.7 mol%, respectively. The sequence of [ELE] can be as the structure carrying long branches and be effective on the rubber-like behavior of the copolymer.

Cases mentioned in above, can strengthen the idea of random distribution of ethylene and propylene units in chain of the copolymer (**MN4**) and can weaken the idea of consecutive monomer units formed in chain of this copolymer.



Scheme 1 Nomenclature used for, **a**, **b**, **c**, **d**, **e**, and **f**) the types of carbons and their sequences; and **g**) the types of branches, xB_n, in the ethylene-propylene copolymer

Methylene sequence lengths

Single succession of ethylene and propylene units such as EPP, PEP, etc. cannot explain the unique carbon sequence. For quantitative study of sequence distribution, ^{13}C NMR data was used to determine the methylene sequence distributions from one to six and longer consecutive methylene carbons [2, 18]. According to the Eqs. (16)–(20), N_i is the moles of methylene sequences with length i. The $S_{\alpha\alpha}$ (peak 1), $S_{\alpha\beta}$ (peaks 8, 9 and 10), $S_{\beta\gamma}$ (peak 22), and $S_{\gamma\gamma}$ (peak 16) are uniquely related to N_1, N_2, N_4, and N_5. N_3 can be estimated from $S_{\beta\beta}$ (peak 25) with a possible check of $S_{\alpha\gamma}$ (peaks 3 and 6) resonance [2].

Table 3 Quantitative analysis and providing comonomer sequences distribution in the copolymer (**MN4**)

Sequences	Molar content (%)
[EEE]	36.5
[PEE + EEP]	trace
[EPE]	17.2
[PEP]	4.6
[PPE + EPP]	2.1
[PPP]	7.8
[PP*P]	trace
[PPP*]	3.1
[PP*PP]	2.4
[P*P*PP]	3.7
1,4-B$_1$ bet E	4.0
1,6-β' B$_1$	11.7
[ELE]	3.2
[E*i*BuE]	1.9
[E2MHE]	1.8

From Eqs. (1) to (15) has been used

$$N_1 = kS_{\alpha\alpha} = kI_1 \tag{16}$$

$$N_2 = k\left({}^1/_2 S_{\alpha\beta}\right) = k\left[{}^1/_2(I_8 + I_9 + I_{10})\right] \tag{17}$$

$$N_3 = kS_{\beta\beta} = kl_{25} = k\left({}^1/_2 S_{\alpha\gamma}\right) = k\left[{}^1/_2(I_3 + I_6)\right] \tag{18}$$

$$N_4 = k\left({}^1/_2 S_{\beta\gamma}\right) = k\left({}^1/_2 I_{22}\right) \tag{19}$$

$$N_5 = kS_{\gamma\gamma} = k\left[{}^1/_2\left(S_{\beta\delta} - S_{\gamma\delta}\right)\right] = k\left[{}^1/_2(I_{23} - I_{18})\right] \tag{20}$$

$$\begin{aligned}\sum_{i=1}^{n} N_i &= k\left[S_{\alpha\alpha} + S_{\beta\beta} + {}^1/_2\left(S_{\alpha\beta} + S_{\beta\gamma} + S_{\beta\delta}\right)\right] \\ &= k\ \left[I_1 + I_{25} + {}^1/_2(I_8 + I_9 + I_{10} + I_{22} + I_{23})\right]\end{aligned} \tag{21}$$

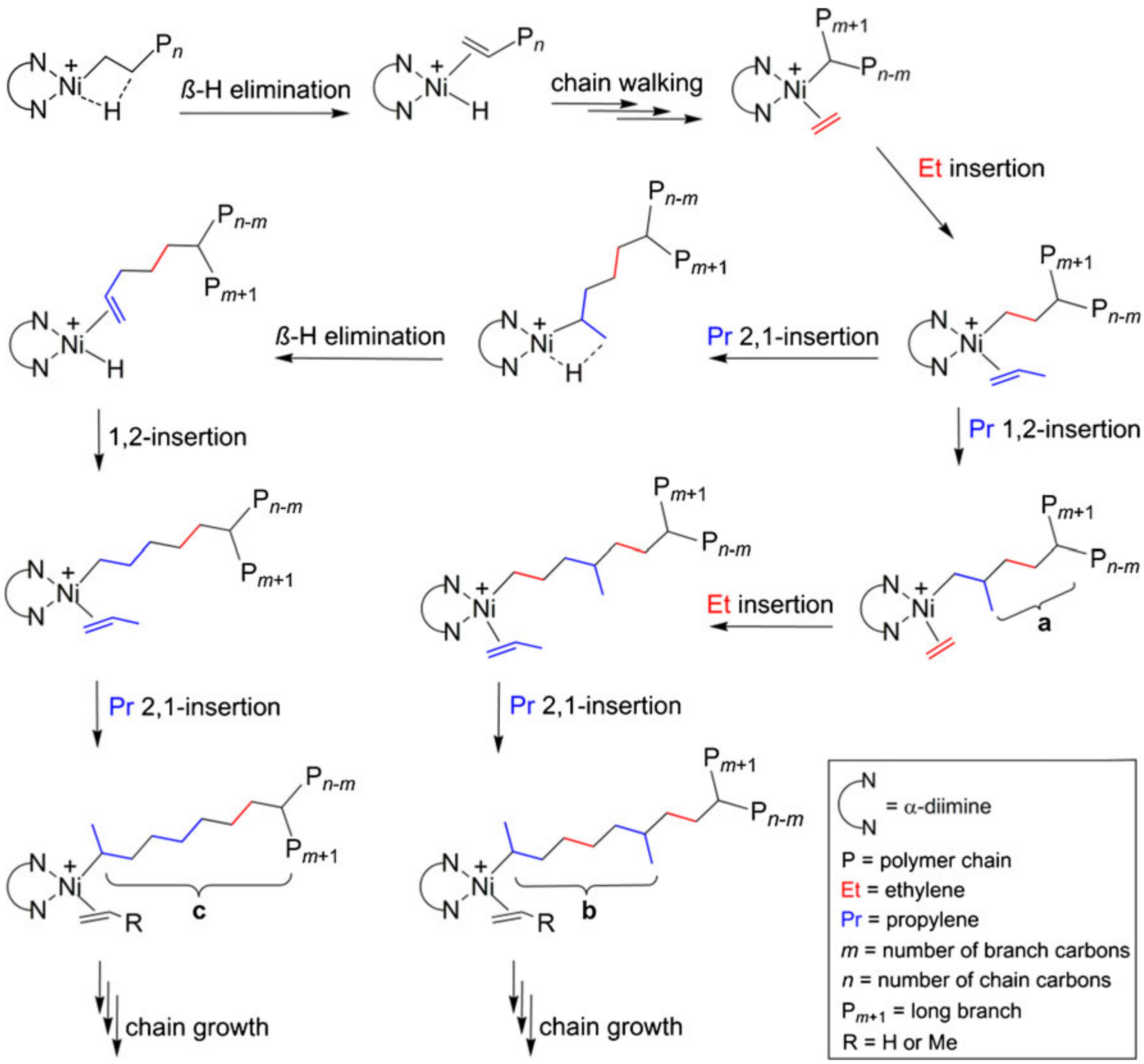
Table 4 Comparison of the copolymer composition and number fractions of uninterrupted methylene sequence for copolymers obtained using the mixed Ni-based (**MN**), vanadium-based (V) and CGC catalyst systems

Sample	F_{Pr}	Et%	$x_{n,1}$	$x_{n,2}$	$x_{n,3}$	$x_{n,4}$	$x_{n,5}$	$x_{n,6+}$	$\sum_{i=1}^{n} x_{n,2i}$	P_{EE}	$\overline{n}_0$	$\overline{n}_{2+}$
MN4	–	59	0.212	0.232	0.095	0.312	0.042	0.107	0.657	0.447	4.39	5.31
V4[a]	0.41	–	0.24	0.15	0.21	0.07	0.11	0.22	0.30	0.52	4.2	5.2
V5[a]	0.50	–	0.30	0.17	0.20	0.08	0.09	0.17	0.32	0.45	3.5	4.6
CGC2[b]	0.308	–	0.382	0.061	0.150	0.021	0.068	0.318	0.133	0.453	5.22	7.82
CGC3[b]	0.321	–	0.394	0.062	0.154	0.020	0.069	0.301	0.128	0.451	4.93	7.49
CGC4[b]	0.583	–	0.595	0.091	0.146	0.019	0.066	0.083	0.127	0.450	2.37	4.39

From Eqs. (16) to (26) has been used

[a,b] Results are obtained from references [16] and [2] respectively

Equation (22) was used to define the number fractions of each sequence while total value $\sum_{i=1}^{n} N_i$ had been estimated previously as Eq. (21) [2]. Also by uninterrupted methylene sequences, is calculated the chain propagation probability for



Scheme 2 Proposed mechanism for short- and long-chain branching and formation of inversion structure (**a**: two consecutive methylene units, 1,4-branch, **b**: four consecutive methylene units, 1,6-branch and **c**: six consecutive methylene units) in ethylene-propylene copolymer chain via ethylene insertion, propylene 1,2- or 2,1-insertion and chain-walking using α-diimine nickel catalyst

ethylene inserted into an active center with terminal monomer group of ethylene (Eq. 23) [2].

$$x_{n,i} = N_i / \sum_{i=1}^{n} N_i \tag{22}$$

$$P_{\mathrm{EE}} = N_5 / N_3 \tag{23}$$

Equation 24 can be used to determine the total number fraction of even methylene sequences [2]. The total number fractions of even methylene sequences for the copolymers obtained using the mixed nickel (**MN**) and vanadium [16] (V) based catalysts and CGC [2] are introduced in Table 4 where F_{P} is the propylene mole fraction in the copolymer.

$$\sum_{i=1}^{n} x_{n,2i} = \frac{\sum_{i=1}^{n} N_{2i}}{\sum_{i=1}^{n} N_i} = \frac{N_2 + \frac{N_4}{1-P_{\mathrm{EE}}}}{\sum_{i=1}^{5} N_5 + \frac{P_{\mathrm{EE}}}{1-P_{\mathrm{EE}}}(N_4 + N_5)} \tag{24}$$

Table 4 shows comparison of the copolymer composition and uninterrupted methylene sequences distributions in the copolymer (**MN4**) (with Et%=59 or Pr%=41) with copolymers obtained by vanadium [16] (V4 with F_{Pr}=0.41 and V5 with F_{Pr}=0.50) and constrained geometry catalyst [2] (CGC2 with F_{Pr}=0.308, CGC3 with F_{Pr}=0.321 and CGC4 with F_{Pr}= 0.584) which Pr% of the copolymer (**MN4**) was in the ranges of propylene content of copolymers obtained by other catalysts.

The $x_{n,1}$, $x_{n,2}$, $x_{n,3}$, $x_{n,4}$, $x_{n,5}$ and $x_{n,6+}$ values in samples produced by each four types of the catalysts with a range of same propylene content were obtained. Alternating propylene-ethylene-propylene sequences can be detected by $x_{n,3}$ which was among the highest concentrations for vanadium EPM samples than CGC and **MN4** EPM copolymers [16]. The $x_{n,2}$ and $x_{n,4}$ results of the copolymer (**MN4**) were higher than those of other copolymers. The higher $x_{n,2}$ and $x_{n,4}$ values in the copolymer (**MN4**) compared to vanadium and CGC EPM samples showed that the inversions in unique microstructure of the copolymer (**MN4**) were higher than other samples. The higher amount of the $x_{n,2}$ in the sample (**MN4**) is due to a significant amount of structures of [PP*PP], [P*P*PP] and 1,4-B_1 between ethylene. The values observed for $x_{n,1}$ and $x_{n,6+}$ reflect the tendency toward block propylene and block ethylene sequences [16]. The results of $x_{n,1}$ and $x_{n,6+}$ of the V EPM samples were lower than those of the CGC EPM copolymers and close to those of the copolymer (**MN4**). In ethylene-propylene copolymerization system using the nickel-based α-diimine catalysts, polymer chain is branched via the insertion of propylene and chain-walking. The nickel-based system can produce inversion structures via propylene 1,2- or 2,1-insertion and chain-walking based on 3,1-enchainment as well as different types of short- and long-chain branches (see Scheme 2) [17, 25–27]. This behavior, formation of more values of inverted propylene by the catalytic system (**MN**) and the results of $x_{n,1}$, $x_{n,2}$, $x_{n,4}$ and $x_{n,6+}$ of the copolymer (**MN4**) showed which the **MN4** EPM sample had more random distribution of ethylene and propylene units than the CGC EPM copolymers. However, the lower $x_{n,3}$ value in the **MN4** EPM sample compared to the other copolymers showed that alternating comonomer sequences were lower than vanadium and CGC samples. The value of the total number fractions of even uninterrupted methylene sequences in the V5 EPM sample was about 32 %, higher than about 13 % which had been reported for EPM obtained from CGC catalyst. The value of this type of methylene sequences in the copolymer (**MN4**) was about 66 %, higher than values of 32 % and 13 % in other copolymers (see Table 4 and Fig. 3).

The value of P_{EE} decreases with decreasing ethylene content of the ethylene-propylene copolymer [2]. The value of P_{EE} in the copolymer (**MN4**) was close to the P_{EE} of copolymers obtained by other catalysts (see EPM samples of Table 4).

The presence of an even number of methylene carbons between methine carbons demonstrates the presence of propylene inversion. With presence of inverted propylene

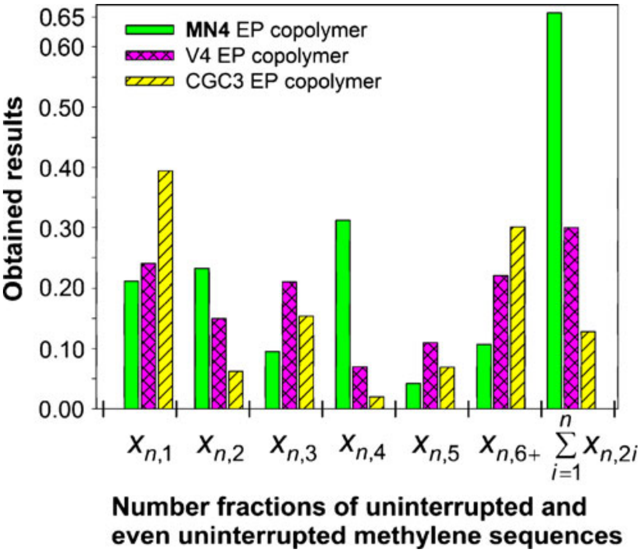


Fig. 3 Comparison of number fractions of uninterrupted methylene sequence and total number fractions of even methylene sequences for copolymers obtained by the mixed Ni-based (**MN4**), vanadium-based (V) and CGC catalyst systems

insertion, is possible to determine the number-average sequence lengths of uninterrupted methylene carbons [16]. The number-average sequence length of uninterrupted methylene carbons $(\overline{n}_0)$ is calculated by Eq. 25 [2]:

$$\overline{n}_0 = \frac{\mathrm{S}_{\alpha\alpha} + \mathrm{S}_{\alpha\beta} + 3\mathrm{S}_{\beta\beta} + 2\mathrm{S}_{\beta\gamma} + {}^5/_2\mathrm{S}_{\beta\delta} + {}^1/_2\mathrm{S}_{\gamma\delta}}{\mathrm{S}_{\alpha\alpha} + \mathrm{S}_{\beta\beta} + {}^1/_2(\mathrm{S}_{\alpha\beta} + \mathrm{S}_{\beta\gamma} + \mathrm{S}_{\beta\delta})} = \frac{I_1 + I_8 + I_9 + I_{10} + 3I_{25} + 2I_{22} + {}^5/_2 I_{23} + {}^1/_2 I_{18} + I_{19}}{I_1 + I_{25} + {}^1/_2(I_8 + I_9 + I_{10} + I_{22} + I_{23})} \tag{25}$$

That $(\overline{n}_0)$ has the same meaning as $(\overline{n}_1)$ here and uninterrupted sequences of two or more methylene carbons $(\overline{n}_{2+})$ is written by Eq. 26 [2]:

$$\overline{n}_{2+} = \frac{\mathrm{S}_{\alpha\beta} + 3\mathrm{S}_{\beta\beta} + 2\mathrm{S}_{\beta\gamma} + {}^5/_2\mathrm{S}_{\beta\delta} + {}^1/_2\mathrm{S}_{\gamma\delta}}{\mathrm{S}_{\beta\beta} + {}^1/_2(\mathrm{S}_{\alpha\beta} + \mathrm{S}_{\beta\gamma} + \mathrm{S}_{\beta\delta})} = \frac{I_8 + I_9 + I_{10} + 3I_{25} + 2I_{22} + {}^5/_2 I_{23} + {}^1/_2 I_{18} + I_{19}}{I_{25} + {}^1/_2(I_8 + I_9 + I_{10} + I_{22} + I_{23})} \tag{26}$$

According to Table 4, the $(\overline{n}_0)$ and $(\overline{n}_{2+})$ values for the copolymer (**MN4**) (41 % propylene) were calculated higher than the samples of V5 (with F_{Pr}=0.50) and CGC4 (with F_{Pr}= 0.583). The values of $(\overline{n}_0)$ and $(\overline{n}_{2+})$ are strongly depended on copolymer composition. Increasing propylene of the copolymer causes decrease the $(\overline{n}_0)$ and $(\overline{n}_{2+})$ values that is because of high incorporation of propylene in the copolymer chains.

Conclusions

Structural analysis of the rubber-like copolymer (**MN4**) obtained by a mixed system (**MN**) containing α-diimine nickel catalysts **n1** and **n2** was completely determined using ^{13}C NMR technique. Triad sequences distribution of [EPE], [PEP] and [PPE + EPP] were about 17.2, 4.6 and 2.1 mol%, respectively. A significant amount of structures with inverted propylene sequences such as [PPP*] (3.1 mol%), [PP*PP] (2.4 mol%), [P*P*PP] (3.7 mol%) and 1,4-B_1 between ethylene units (4.0 mol%) and structures of long branches (3.2 mol%) and 1,6-β B_1 (11.7 mol%) in the unique microstructure of the **MN4** EPM copolymer were detected and calculated. The number fractions of uninterrupted methylene sequence in the copolymer (**MN4**) were compared to those in the copolymers obtained using vanadium-based Ziegler-Natta and CGC catalysts. The results indicated that the copolymer (**MN4**) had fewer alternating comonomer units than copolymers obtained by the vanadium and CGC catalysts while the **MN4** EPM copolymer had more random distribution of ethylene and propylene units than the CGC EPM samples. The total number fractions of the even uninterrupted methylene sequences that could indicate the inversion structures in the copolymer (**MN4**) with unique microstructure were about 66 %, higher than values of 13 % and 32 % reported for copolymers obtained from CGC and vanadium-based catalysts, respectively.

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