DOI: 10.1002/masy.200851405

Statistical Distribution Analysis of Polypentenamer cis–trans Structural Units

Fadhel Ismail,[1] Farida Bendebane,[1] Lamia Bouziane,[1] Abbés Boukhari[2]*

Summary: The polypentenamer studied in this work, was a product obtained from bulk polymerization of gaseous cyclopentene into condensed polymer in presence of tungsten hexachloride alone as catalyst without any other reagent. This linear polymer doesn't present cross-links or detectable secondary ramifications. However, its structural unit presents a double bond which can be in different configurations corresponding to cis and trans geometric isomers. The objective of this study was to determine the distribution type of these different structural units constituting the polymer chains. Fractions of cis and trans structural units in polymer chains were calculated from ^{13}CNMR spectra. Statistical distribution of these structural units was observed on high resolution ^{13}CNMR spectra, with the apparition of a quadruplet and a triplet corresponding respectively to the carbon on α and β position. The sextuplet corresponding to the carbon of the double bond was observed clearly in this work (may be because the product polymer is very pure), and confirms the statistical distribution. All peaks corresponding to the different positions of the α-carbon, the β-carbon and the olefinic carbon in polymer chains were attributed from statistical analysis of the polypentenamer microstructure.

Keywords: cis-trans; microstructure; polypentenamer; statistical distribution

Introduction

The polypentenamer, poly(1-pentenylene) or also called polycyclopentene (PCP) is a polymer obtained by ring opening reaction of cyclopentene (ROMP: "Ring Opening Metathesis Polymerization"). This unsaturated linear product does not present detectable reticulations or secondary ramifications.[1–7] The double carbon-carbon bond in the structural repeat unit gives polymer cis and trans geometrical configurations (Figure 1).

PCP was synthesized for the first time on 1957 by Eleuterio.[1] Then, Natta[2] on 1964 using another catalytic system, observed the cis and trans configurations of the double bond by IR spectroscopy (the metathesis reaction had not yet known). PCP is a good general purpose rubber whose vulcanized products are comparable with those of polybutadiene or polyisoprene. However, it has no special or unusual properties to compensate for its more expensive production. This is why PCP did not become a commercial product until recently. But in research, it is interesting as an intermediate product; for example, an easy method was developed for the synthesis of narrow-distribution defect free linear polyethylene, this polymer was obtained via catalytic hydrogenation of polypentenamer.[3] In the same way, unsaturated fluorinated and cyclopentene copolymers prepared by ROMP were 99% hydrogenated to give new products of saturated material showing lower Tg values.[8]

In ROMP, most catalysts used are homogeneous systems, but there are also a few heterogeneous catalytic systems which are very effective. However, heterogeneous catalytic systems did not attain

---

[1] Department of Chemical and Process Engineering, University Badji-Mokhtar Annaba, Algeria

[2] Department of Chemistry, University Badji-Mokhtar Annaba, Algeria
Fax: (+213) 38 876560;
E-mail: ismail.fadhel@univ-annab.org

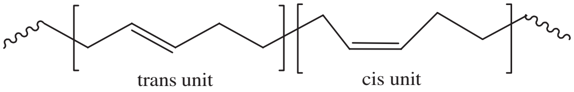

Figure 1.
Polypentenamer.

much application in ROMP, where as homogeneous catalysts are very important. Catalytic systems are complexe, they are generally composed of catalysts (WCl_6, WF_6, $MoCl_5$, $R_2CW(CO)_5$, etc.), cocatalysts ($EtAlCl_2$, $SnEt_4$, $TiCl_4$, $Al(isobut)_3$ etc.), and activators (ROR, ROH, RCOOR, RNH_2 etc.). Sometimes, a little olefinic molecule is used to initiate the polymerization of the cycloolefin, indeed it has an effect on the molar mass of the product, and on the rate of the reaction.[9] A special group of metathesis catalysts is based on individual organometallic compounds of W, Mo, which are the carbenic complexes of transition metals. Pentacarbonyl tungsten methoxyphenylcarbene, pentacarbonyl tungsten diphenylcarbene and tetracarbonyl tungsten methoxybutenylcarbene, were used without any cocatalyst in cycloolefin metathesis polymerization.[10–12] Another group of effective homogeneous catalysts for metathesis polymerization of cycloolefins was subsequently developed on the basis of stable carbenes of tungsten and molybdenum.[13,14] The formation of transition metal carbene complexes in metathesis polymerization initiated by Ziegler type and similar multicomponent catalytic systems is not completely understood. The reaction between the two main components of the catalytic systems first occurs in the same way as in typical Ziegler systems to give a metal organic intermediate with a δ-transition metal-carbon bond. Rather, it is shown that the higher molecular weight material in PCP originates in a secondary metathesis reaction: intermolecular acyclic metathesis between the metal carbene chain end and the C=C double bonds which are present in PCP chains.[6] Acyclic metathesis competes with the ROMP of CP in the presence of $Mo:PMe_3$ as catalyst system. The ratio of rate constants for propagation versus acyclic metathesis is 1600 approximately.[7]

The polypentenamer studied in this work, is a product obtained from bulk polymerization of cyclopentene in gas phase and in presence of tungsten hexachloride alone as catalyst without any other reagent.[15] The conversion of gaseous monomer to condensed polymer was studied kinetically and the polymer thus formed, was analyzed by GPC (gel permeation chromatography) technique, ^{1}HNMR and ^{13}CNMR spectroscopy. The gas phase polymerization was defined as the conversion of pure gaseous monomer into polymer in the condensed phase. The main objective of this work is to determine the type of distribution of these structural units within chains constituting polymer.

Structure of Polymer

Linearity of Polymer

The analysis of the polymer by ^{1}HNMR is carried out on a Varian XL-200 apparatus (200 MHz), in deutered chloroform containing TMS as reference. Spectra of cyclopentene and polypentenamer show a certain similarity relating the conservation of the ethylene character of the monomer in the produced polymeric chain. Indeed, the fraction of the ethylene protons compared to the protons in α position and those in β position are the same in the monomer and in polymer. The curves of integration given by the apparatus, show a ratio of 1/2/1 correspondent to β, α and olefinic protons in both monomer and polymer. Moreover, no peak shows the presence of asymmetrical carbon proton (absence of reticulations in polymer). The difference between the two spectra is located initially in the light translations of the chemical shifts of all

Table 1.
H NMR of cyclopentene (CP), polypentenamer (PCP) experimental and theoretical model.

Assignment		Chemical shift (ppm)		
		CP experimental	PCP*	experimental theoretical
H–C=C	(cis)*	5.74	5.37	5.42
	(trans)*		> 5.37	5.48
H–C–C=C		2.32	2.00	1.96
H–C–C–C=C		1.82	1.40	1.37

peaks of polymer compared to monomer (monomer: 5.74 ppm, 2.32 ppm and 1.82 ppm; polymer: 5.37 ppm, 2.00 ppm and 1.40 ppm), and especially in the appearance of cis-trans geometrical isomerization on the proton of the polymer double bond;[16] the enlarging of the peak at 5.37 ppm shows clearly two closer peaks. Indeed, it is checked by the application of a software program (ACD, Chem. Off. 2004) on an ideal simulated model which gives peaks at 1.37 ppm and 1.96 ppm for β and α hydrogen, and two other peaks brought closer to 5.48 ppm and 5.42 ppm corresponding respectively to trans and cis olefinic hydrogen (Table 1).

Isomerization of Polymer

The isomerization cis-trans of the double bond of the polypentenamer and which depends on temperature,[17–20] is confirmed by ^{13}CNMR. Indeed, results obtained on a Bruker WP-80 apparatus (22.63 MHz), show clearly a difference between spectra of cyclopentene and polymer (Figure 2,3); the spectrum of cyclopentene presents three peaks corresponding to carbons of the double bond (130.82 ppm), α position (32.63 ppm) and β position (23.04 ppm), whereas on the polymer spectrum, other peaks appear indicating the presence of cis and trans isomer units. Thus, olefinic carbon gives two peaks at 130.02 ppm and 130.53 ppm correspondent respectively to cis and trans units. Carbon in α position compared to the cis or trans units, presents also two peaks at 26.99 ppm and 32.12 ppm respectively. Lastly, carbon in β position which is not affected by the cis-tans isomerization of the double bond, presents only one peak at 29.92 ppm. That is consolidated by the simulated ideal model (Figure 4) which gives the same information for carbons in β position (29.9 ppm), in α position cis (27.8 ppm) and tans (33.8 ppm). But this model remains still insufficient to distinguish between cis and trans units of the olefinic carbons (Table 2).

Microstructure of Polymer

At weak resolution, ^{13}CNMR cannot detect the difference between a mechanical mixture of cis and trans homopolymer chains, and copolymer chains in which the cis and trans units are statistically distributed.[21,22] However, at higher resolution, it becomes

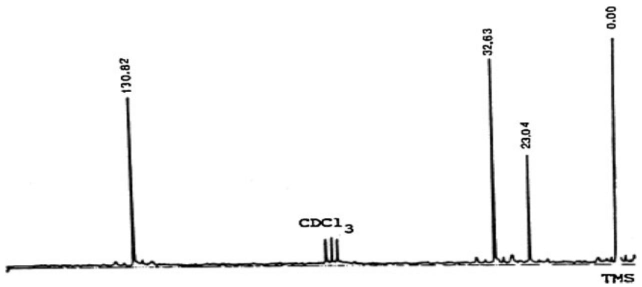

Figure 2.
^{13}C NMR Spectrum of cyclopentene at 22,63 MHz.

very interesting; a long distance coupling takes place and produces n-ades phenomenon which is due to the geometries of the two double bonds situated on both sides of concerned carbon.[23] Indeed, the spectrum of polymer obtained on "Varian XL-200" NMR apparatus, presents:

– for carbon in β position, three peaks at 29.57 ppm, 29.73 ppm and 29.86 ppm correspond to the three possible positions between the two double close bonds of isomer units. This phenomenon indicates that polymer chains are made of cis and trans structural units statistically distributed (triplet in Figure 5).

– for carbon in α position, a quadruplet made up of two doublets located on both sides of the β-carbon triplet, at 26.76 ppm, 26.90 ppm, 32.10 ppm and 32.22 ppm, corresponds to the four possible positions of α-carbon between two adjacent isomer double bonds. This phenomenon which does not appear at weak resolution, confirms the statistical distribution of structural isomer units in polymer chains.

Figure 4.
^{13}C NMR assignments for polypentenamer simulated model (cis-trans fraction).

– for olefinic carbon, a sextuplet made up of two triplets around 129.84 ppm and 130.30 ppm corresponding respectively to cis and trans isomers, with a very long distance coupling (Figure 6). This phenomenon confirms once again the statistical distribution.

The software "Chem.Office 2004, Ultra Chem.Draw 8.0" treating ideal models, does not make distinction between homopolymer chains and copolymer chains for cis-trans polypentenamer (Figure 4). This program remains still insufficient to interpret such structure and thus it requires better performance.

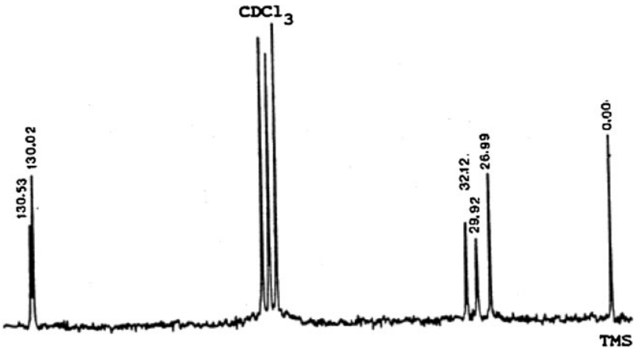

Figure 3.
^{13}C NMR Spectrum of polypentenamer 62% cis at 22,63 MHz.

Table 2.
^{13}C NMR of cyclopentene (CP), polypentenamer (PCP) experimental and theoretical model.

Assignment		Chemical shift (ppm)		
		CP theor. & exp.	PCP*	
			experimental	theoretical
C=C	(cis)*	130.82	130.02	128.2
	(trans)*		130.53	
C–C=C	(cis)*	32.63	26.99	27.8
	(trans)*		32.12	33.8
C–C–C=C		23.04	29.92	29.9

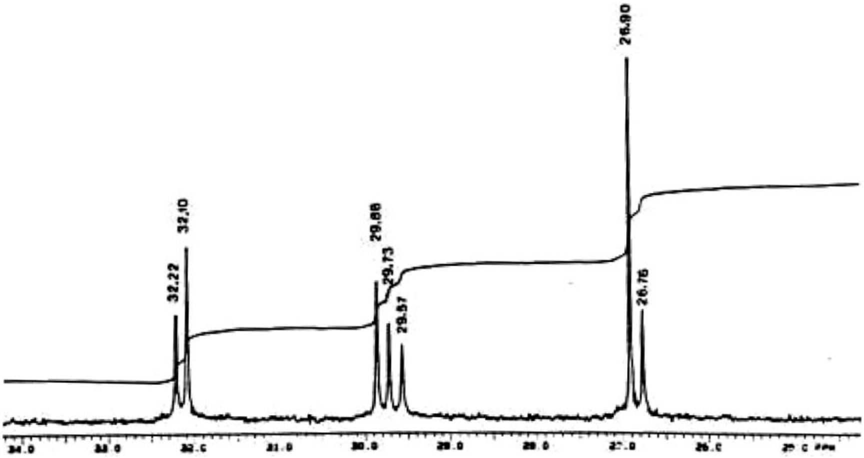

Figure 5.
Enlargement of ^{13}C NMR Spectrum of polypentenamer (62% c **g**is) at 50 MHz (peaks corresponding to carbons in α and β position).

Statistical Analysis

As it is a polymer chains consisting of copolymers containing isomer basic units, a statistical study is needed to determine the distribution of these units inside chains. This study would probably make it possible to allot peaks and chemical shifts with carbons according to various possible combinations of their sites in the chain.

P_c and P_t are the probabilities of finding cis and its geometrical trans isomer respectively within the same chain. These probabilities correspond obviously to the fractions of cis and trans units which can be calculated from different spectra (63.7% cis, using Bruker WP-80 apparatus (Figure 3) and 61.4% cis, using Varian XL-200″ apparatus (Figure 5,6)).

Analysis of the β-carbon triad: P_{cc}, P_{tt} and P_{ct} or P_{tc} are the probabilities of finding two successive cis units, two successive trans units and alternated cis-trans units respectively. If the distribution of isomer structural units corresponds to Bernoulli

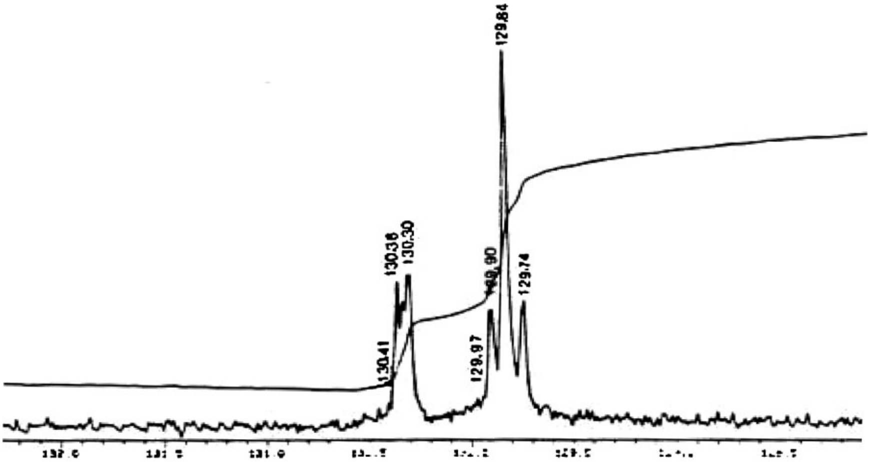

Figure 6.
Enlargement of ^{13}C NMR Spectrum of polypentenamer (62% cis) at 50 MHz (peaks corresponding to the olefinic carbon).

Table 3.
Probabilities of distributions and attributions of β-carbon peaks.

$P_c = 0.614$	P_{cc}	$P_{ct} = P_{tc}$	P_{tt}	P_c	P_t
Bernoulli process	0.377	0.474	0.149	**0.614**	***0.386***
Applied Bp	0.310	0.448	0.242	0.543	*0.466*
Observed	**0.448**	**0.310**	**0.242**	**0.603**	***0.397***
δ (ppm)	***29.86***	***29.73***	***29.57***		

process (Bp), these probabilities should be expressed by the following equations:

$$P_{cc} = (P_c)^2$$

$$P_{tt} = (P_t)^2$$

$$P_{ct} = P_{tc} = 2P_cP_t$$

$$P_c = P_{cc} + (P_{ct})/2 = (P_c)^2 + P_cP_t$$

$$P_t = P_{tt} + (P_{tc})/2 = (P_t)^2 + P_cP_t$$

The values obtained according to this theory are compmared with those calculated from the experimental spectrum (Table 3). Two combinations award peaks of the triad are then studied (the other combinations are unsuitable in view of eye): Following the logic of Bernoulli by allotting peaks according to the order of magnitude of the values pre-established by the statistics (Applied Bp), experimental calculations of P_c and P_t ($P_c = 0.534$, $P_t = 0.\ 466$) from spectrum, do not concord with confirmed values ($P_c = 0.614$, $P_t = 0.\ 386$). However, the second combination that is different from Bp, gives interested values; 0.603 for P_c and 0.397 for P_t, compared respectively to 0.614 and 0.386. Furthermore, the values of P_{cc}, P_{tt}, and P_{tc} P_{ct} determined from the spectrum will concord to those observed on the of α-carbon triad (next section).

These above results show thus, that P_{cc} and P_{tt} probabilities are larger and P_{ct} probability is weaker than respectively those calculated according to Bernoulli process (BP). The chemical shifts corresponding to the three peaks of β-carbon ^{13}C NMR Spectrum of the polypentenamer, are then given according to the geometrical model on the Figure 7 representing the position of β-carbon between the two adjacent possible isomer units.

Analysis of the α-carbon triad: The ^{13}C NMR Spectrum of α-carbon is not only affected by the nearest double bond but also by the second close double bond which surrounds it. According to Bernoulli statistics, this analysis would be slightly different compared to the preceding study; there is no symmetry of the α-position carbon. The different probabilities should be expressed by the following equations[21]:

$$P_{cc} = (P_c)^2$$

$$P_{tt} = (P_t)^2$$

$$P_{ct} + P_{tc} = 2P_cP_t$$

$$P_c = P_{cc} + P_{ct}$$

$$P_t = P_{tt} + P_{tc}$$

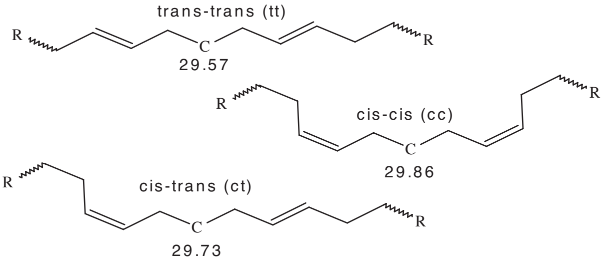

Figure 7.
Chemical shifts of β-carbon on the polypentenamer ^{13}C NMR Spectrum.

Table 4.
Probabilities of distributions and attributions of α-carbon peaks.

$P_c = 0.614$	P_{cc}	P_{ct}	P_{tc}	P_{tt}	P_c	P_t
Bernoulli process	0.377	0.273	0.237	0.149	**0.614**	***0.386***
Observed	**0.485**	**0.144**	**0.140**	**0.231**	**0.629**	***0.371***
δ (ppm)	***26.90***	***26.76***	***32.22***	32.10		

For each cis-trans position of one α-carbon, corresponds automatically a trans-cis position of the other α-carbon, thus $P_{ct} = P_{tc}$. In this case, the attribution of the peaks is directed; indeed, the two peaks on both sides and which have the same intensity correspond obligatorily to P_{ct} and P_{tc}, however, the two others correspond to P_{cc} and P_{tt} according to their respective areas (Figure 5). Only one combination of attribution is possible, showing clearly that the statistical distribution is not perfect (Table 4). The same phenomenon of successions of identical units is once again observed as in the preceding analysis of β-carbon; P_{cc}, P_{tt} are greater and P_{ct}, P_{tc} are weaker than those envisaged by Bernoulli. The values of P_{cc}, P_{tt}, P_{ct} and P_{tc} observed on this α-carbon spectrum agree well with β-carbon attributions.

The chemical shifts corresponding to the three peaks of α-carbon ^{13}C NMR Spectrum of the polypentenamer, are then given according to the geometrical model on the Figure 8 representing the position of α-carbon between the two adjacent possible isomer units.

Analysis of the olefinic carbon: The two triplets of the sextuplet, at 129.84 ppm and 130.30 ppm correspond to the olefinic carbons of the cis and trans isomer structural units respectively. This is a very long distance coupling; indeed, the carbon of the double bond can be located between two adjacent double bonds which can also take cis or trans different geometries and this is why there are six peaks in Figure 6 corresponding to six combinations of possible positions as shown in Figure 9.

The statistical analysis of this sextuplet is more complicated, as it is a tetrad, in addition to the application of statistical Bernoulli, the first order Markov can also be applied. That will be the subject of an article to be published shortly. This analysis confirms that this distribution is not perfectly and doesn't obey any more to the first-order Markov process, but the combination of the two processes allows to the results showing in Table 5.

Discussion

For this kind of polymer, we can determine the average number of structural units for forming a base sequence (N):

$$N = (P_{ct})^{-1} = (Nc + Nt)/2$$

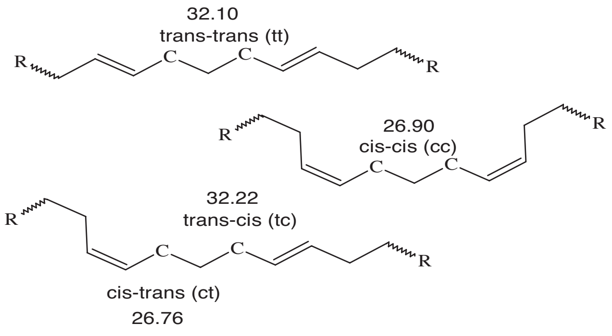

Figure 8.
Chemical shifts of α-carbon on the polypentenamer ^{13}C NMR Spectrum.

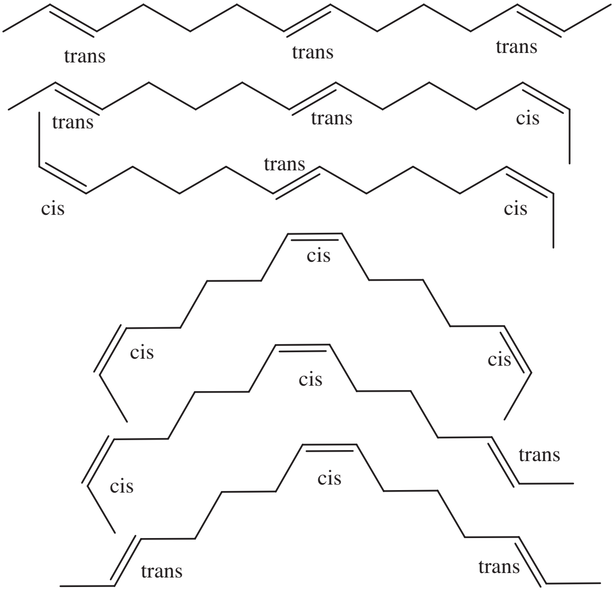

Figure 9.
Distributions of a double bond between two adjacent double bonds.

Table 5.
Probabilities of distributions and attributions of olefinic carbon peaks.

Distribution	ctc	ttt	ctt	tct	ccc	cct
Probability	0.139	0.121	0.145	0.110	0.363	0.121
δ (ppm)	130.41	130.36	130.30	129.90	129.84	129.74

Where Nc and Nt successively represent average numbers of cis and trans units for both types of sequences corresponding. These numbers are determined from the following equations[16]

$$Nc = 1 + 2P_{cc}/P_{ct}$$

$$Nt = 1 + 2P_{tt}/P_{ct}$$

The application of these equations on the polymer studied using the probabilities experimentally determined and the results are:

$$Nc = 3.89;\quad Nt = 2.56;\quad N = 3.23$$

These values are consistent with the results of probabilities proposed for the olefinic carbon tetrad, because the peak corresponding to P_{ccc} (the following of three cis units), is the most intense since the average number Nc exceeds the value three. The peak corresponding to P_{ttt} can not be intense as long as Nt which is less than three (there is not much estates of three trans units). Each polymer according to its percentages in cis and trans units must have its own average values of these numbers. Conversely, if the polymer had a perfectly statistical distribution (bernoullian), average numbers of its frames are:

$$(Nc)_o = 2.59;\quad (Nt)_o = 1.63;\quad (N)_o = 2.11$$

Conclusion

The polypentenamer studied in this work, is gotten from bulk polymerization in gaseous phase of pure cyclopentene in presence of only tungsten hexachloride as catalyst without any other reagent. Fractions of cis and trans structural units in polymer chains, are calculated from ^{13}CNMR spectra. Statistical distribution of these structural units is observed on ^{13}CNMR spectra, with apparition of a quadruplet and a triplet corresponding to the carbon on α and β-position respectively, and a sextuplet corresponding to the carbon of the double bond. Following the analysis of the polymer by ^{13}CNMR spectroscopy, a long-range coupling is found. The spectra are very significant so the polymer is pure and has no reticulation or imperfection. The peaks of α and β carbons are awarded by means of a statistical study. The distribution of these isomer structural units within the polymer chains is not perfectly statistics, and doesn't obey any more to the first-order Markov process. However, the combination of the bernoullian statistics with the first order of Markov process, permit to attribute the six peaks of the olefinic carbon according its location between the double bonds that surround it in polymer chains.

In the literature, the dependencies of the proportion of isomers units within the polymer are generally similar to that found in this work, although they vary depending on the catalytic systems used and the operating conditions. All these polymerizations should follow probably a general rule as a statistical law in which contributions from different levels could be added.

Active species at the end of the chain which allow the propagation of the polymer, have probably a temporal selectivity for species with same geometrical structure, and as a function of temperature, the opening of cyclopentene produces a cis or trans pentenyle. This phenomenon should explain the high values of probabilities of succession cis-cis and trans-trans units.

Finally, at this level we arrive to the most delicate problem, because these contributions should depend strongly on the general mechanism of polymerization which is still poorly understood. We don't need only to know the mechanism of propagation, but also the boot giving active species and their stabilities which apparently must manage the ring opening and the polymerization initiation.

[1] Ger. Pat. 10728110 (**1960**), Formation of insaturated polymers, H.S. Eleuterio.

[2] G. Natta, D. Dall'Asta, G. Mazanti, *Angew. Chem.* **1964**, *76*, 765–777.

[3] S. T. Trzaska, L. B. W. Lee, R. A. Register, *Macromolecules* **2000**, *33*(25), 9215–9221.

[4] M. Gimeno, Synthesis and characterization of potentially electrostrictive polymers, PhD thesis, Durham University, **2002**.

[5] W. J. Feast, M. Gimeno, E. Khorsavi, *Journal of molecular Catalysis A: Chemical* **2004**, 2139–2144.

[6] G. Black, D. Maher, W. Risse, Living ring-opening metathesis polymerization, in *Handbook of metathesis Applications in polymer synthesis*, vol. 3, R. H. Grubbs, Ed., Wiley, Weinheim **2003**, 2–71.

[7] L. B. W. Lee, R. A. Register, *Polymer* **2004**, *45*, 6479–6485.

[8] W. J. Feast, M. Gimeno, E. Khorsavi, *J. Mol. Cat.* **2004**, A Chem., *213*, 9–14.

[9] T. J. Katz, S. J. Lee, M. Nair, E. B. Savage, *J. Am. Chem. Soc.* **1980**, *102*, 7940–7942.

[10] C. P. Casey, T. J. Burkhardt, *J. Am. Chem. Soc.* **1973**, *95*, 5833–5834.

[11] C. P. Casey, T. J. Burkhardt, C. A. Bunnell, J. C. Calabrese, *J. Am. Chem. Soc.* **1977**, *99*, 2127–2134.

[12] T. J. Katz, N. Acton, *Tetra. Let.* **1976**, *17*, 4247–4251.

[13] J. Kress, J. A. Osborn, *J. Am. Chem. Soc.* **1983**, *105*, 6346–6349.

[14] R. R. Schrock, *J. Organomet. Chem.* **1986**, *300*, 249–257.

[15] F. Ismail, A. Boukhari, R. Kherrat, L. Tifouti, *Iranian Polymer Journal* **2006**, *15*(2), 169–177.

[16] O. Dereli, B. Düz, Y. Imamoglu, *European Polymer Journal* **2006**, 42, 368–374.

[17] J. Léonard, *Macromolecules* **1969**, *2*, 661.

[18] Bui Van Tam, thèse de Doctorat, Université Laval, **1977**, 17–21, 51–60.

[19] B. V. Lebedev, I. B. Rabinovich, Vya Lityagov, *Dokl. Akad. Nauk, SSSR* **1977**, *237*, Eng. 1115.

[20] F. Ismail, F. Bendebane, A. Boukhari, *CNRS Libanease Sciences Journal* **2008**, in press.

[21] F. Bovey, Chain Structure and Conformation of Macromolecules, Academic. Press, **1982**.

[22] P. Dounis, W. J. Feast, A. M. Kenwright, *Polymer* **1995**, *36*, 2787.

[23] K. J. Ivin, J. C. Mol, Olefin metathesis and metathesis polymerization, Academic Press, London **1997**.