

Dependence of the structural parameters and properties of low density polyethylene on the synthesis conditions

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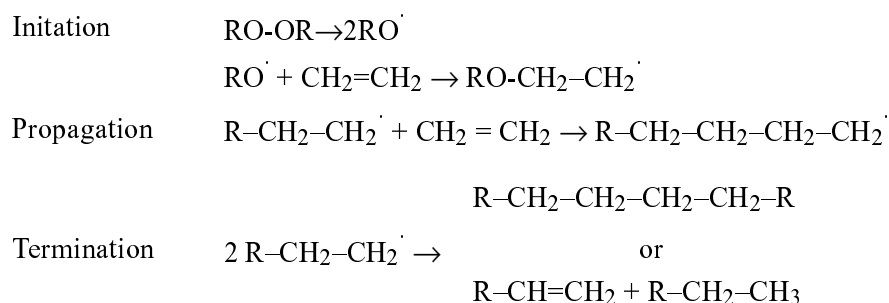
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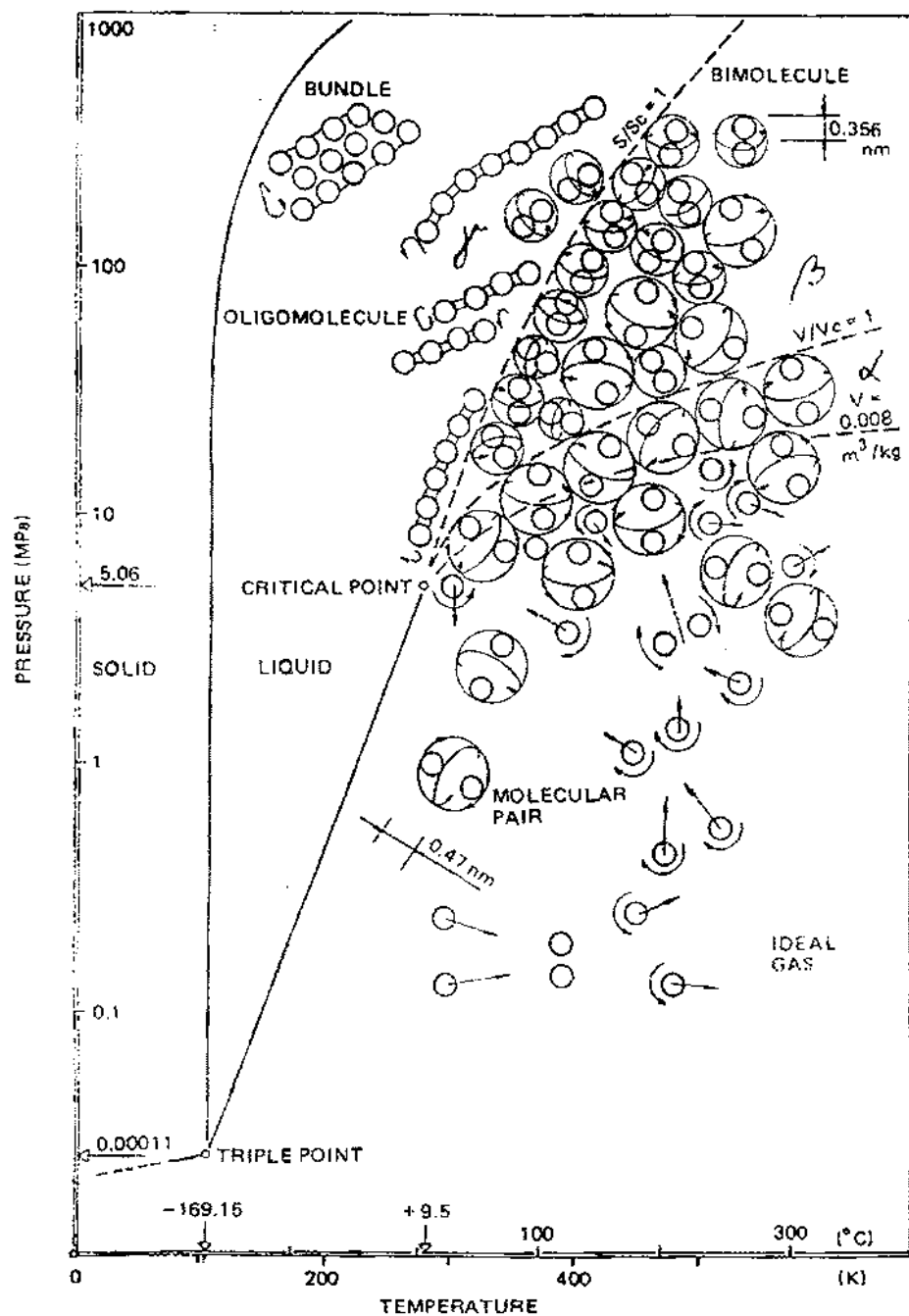
In a previous publications from the authors' laboratory a method was developed to predict the structure and properties of low density polyethylene (PE-LD) that could be obtained over a very wide range of polymerization conditions. The method was proved using experimental data from the literature. However, some shortcomings of the method were noticed. The aim of this work was to overcome the shortcomings and to enable the better manipulation of experimental data using a computer. A computer program has been developed to establish the mathematical relationships between ethylene entropy and the structural parameters and density of PE-LD. All available experimental data (more than 300 experimental points) have elaborated and confirmed our mathematical models and our theoretical predictions.

Key words: low density polyethylene, structure, properties, mathematical model.

Ethylene is polymerized by a free radical mechanism under reaction conditions (100–350 MPa, 423–573 K) fairly above the conditions of the critical point (5.06 MPa and 282.65 K):



Since the polymerization temperature is significantly higher than the critical one, it is usual to consider that the ethylene is in gas phase even when the pressure is very high. The density of ethylene under the polymerization conditions, however, is 400–500 kg/m³, close to the value of liquid ethylene. The density of compressed

Fig. 1. Phase state of compressed ethylene.⁶

ethylene is higher than the density of randomly packed ethylene molecules (280 kg/m^3). So, it can be concluded that the ethylene molecules are closely and regularly packed under the polymerization conditions.

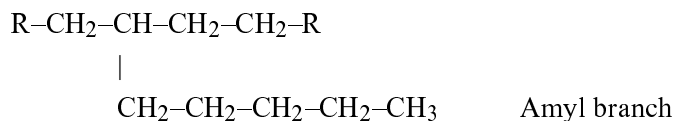
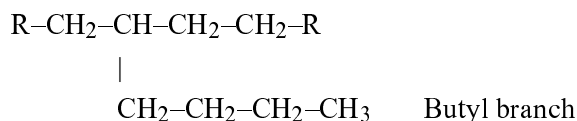
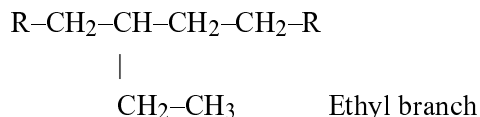
Ethylene molecules under high pressures are packed into various supermolecular particules.¹⁻³ There are three phases in compressed ethylene (Fig. 1): the α -phase (consisting of a mixture of single molecules and molecular pairs), the β -phase (rotating molecular pairs and bimolecules) and the γ -phase (rotating bimolecules, oligomolecules and oligomolecular bundles). With the change of the state of the ethylene from an ideal gas to the γ -phase, the degree of order on the supermolecular level is also changed. The molecules are highly organized in γ -phase but not in α -phase or β -phase of ethylene. Hence, the entropy of γ -ethylene is very low. The entropies of α -ethylene and β -ethylene are higher than the entropy of γ -ethylene.²

According to the classical explanation of a free radical polymerization, a monomer molecule is attached to the macroradical, thus forming one-by-one repeats of the macromolecular chain. Due to the supermolecular organization of compressed ethylene, however, it is proposed that a one-by-one supermolecular particle is attached to the macroradical (or a primary radical formed in the initiation reaction) thus forming a segment-by-segment of the macromolecular chain.⁴ In this case, different reactivities of various supermolecular species toward the free radicals are to be considered. Not only the differences in the reactivity of various supermolecular species but also their relative concentrations under different polymerization conditions (pressure and temperature) should be taken into account. Low reactive molecular pairs dominate in the α -phase. Very reactive bimolecules dominate in the β -phase, but the highest concentration of them are encountered near the β - γ transition. Oligomolecules prevail in the γ -phase.

The supermolecular structure of monomer has a decisive effect on the polymerization rate. The structure of a macromolecular chain must be an authentic reflection of the original chain process. In the case of an organized monomer system, the lifetime of a macroradical is composed of subsequent periods of rapid growth and stagnation.⁴ The period of rapid growth arises when a macroradical begins to connect monomer molecules that belong to a supermolecular particle. Once all the molecules from that particle are bound into the macromolecular chain, a period of stagnation begins. During the stagnation a macroradical can isomerise or collide with other particles present in the system (impurities, chain transfer agents, comonomer, polymer, *etc.*). As a consequence, processes leading to structural impurities (branches, unsaturation, termination, copolymerization, *etc.*) in the molecular chain arise. The concentrations of these structural impurities in the polyethylene chain (per 1000 carbon atoms) should be inversely proportional to the degree of organization of the ethylene molecules.^{3,4}

The basic structural characteristics of low density polyethylene (PE-LD) macromolecules are short and long chain branches (with more than five carbon atoms in the chain), unsaturated bonds, molecular mass and its distribution. These

characteristics have decisive effects of PE-LD properties, such as density and melt flow rate (MFR). Less branched PE-LD is characterized by a higher density. PE-LD with a lower molecular mass has a higher MFR. Density and MFR have decisive effects on the processing and application of PE-LD. In a molecule of PE-LD ethyl, butyl and amyl branches exist as the short branches:



Vinylidene ($\text{CH}_2=\text{C}<$) and transvinylidene ($-\text{CH}=\text{CH}-$) bonds exist in a molecule of PE-LD as unsaturated impurities.

The effect of the synthesis conditions on the macromolecular structure and properties of PE-LD are usually considered in the relation to the pressure and temperature of the polymerization reaction.⁷⁻¹¹ Our starting point, however, is that neither pressure nor temperature but the entropy of the compressed ethylene is crucial for the PE-LD structure and properties. It was shown that in spite of the very great differences in the polymerization conditions (tenfold increase of pressure, wide temperature range and different methods of initiation), equal macromolecular structure and properties of PE-LD are obtained if the entropy of the compressed ethylene is constant.¹⁻⁶

In previous papers^{1,2,4} from author's laboratory, the effects of the ethylene entropy on the short (ethyl, butyl and amyl) and long branches, unsaturated bonds and density of PE-LD were expressed by mathematical equations derived by regression analysis of empirical data. A method was developed to predict the structure and properties of PE-LD that could be obtained over very wide range of polymerization conditions. This method has been accepted by some other researchers.^{12,13}

There are some shortcomings, however, in the derived equations:

1. Only linear mathematical expressions (or those that can be transformed to linear ones) were used. (Non-linear expressions could give better results).

2. The entropy of compressed ethylene at the polymerization pressure and temperature was estimated graphically using the well-known Benzler-Koch diagram.⁵ (Entropy can be estimated more precisely if it is calculated by Benzler-Koch method.)

3. A statistical estimation of the validity of each experimental point was not performed. It was obvious that some points are not quite correct; *i.e.*, these points could be experimental error. (Better results would be obtained if the incorrect points were rejected.)

The purpose of this work was to overcome these shortcomings and, to enable the better manipulation of experimental data, by the use of a computer.

COMPUTER PROGRAM DEVELOPMENT

To overcome the shortcomings, a computer program was developed to find reliable mathematical expressions to describe the dependence of different PE-LD structural characteristics and properties on the entropy of ethylene under the polymerization conditions.

Using the developed computer program:

1. Data input is very simple (ethylene pressure, temperature and the value of the specific structural characteristic).

2. Data could be added, deleted, stored and printed.

3. The ethylene entropy under the polymerization conditions (pressure and temperature) is calculated exactly using the Benzler-Koch method.

4. Any type of equation (linear and non-linear) can be used to fit the data and to determine the correlation between ethylene entropy and the structural characteristic of PE-LD density.

5. A graphical presentation of the data, combined with the regression curve, is plotted in diagrams "Ethylene entropy vs. the value of the structural characteristic (or PE-LD density)".

6. Each experimental point can be evaluated and rejected if do not fit to the obtained regression curve.

7. Prediction of the structure and density of PE-LD for any polymerization pressure and temperature (above the critical point values, *i.e.*, 5.06 MPa and 282.65 K) is possible.

ELABORATION OF EXPERIMENTAL DATA USING DEVELOPED COMPUTER PROGRAM

Available published data have been collected^{6,14-23} (more than 300 experimental points) about the effects of ethylene pressure and temperature on the structure and density of PE-LD. (All of them are stored in our computer program.) The data were subjected to regression analysis using the next eleven types of mathematical expressions (but any other type can be included).

$$F = a + bS \quad (1)$$

$$F = a + bS + cS^2 \quad (2)$$

$$F = a + bS^3 \quad (3)$$

$$F = a + bS + cS^2 + dS^3 \quad (4)$$

$$F = a + bS + cS^2 + dS^3 + eS^4 \quad (5)$$

$$F = a + b/S \quad (6)$$

$$F = (1 + bS)/(c + dS) \quad (7)$$

$$F = (a + bS + cS^2)/(d + eS + fS^2) \quad (8)$$

$$F = a + b/S + c \log(S) + dS \quad (9)$$

$$F = \exp^{(a+bS)} \quad (10)$$

$$F = \exp^{a+b/S+c \log(S)+dS} \quad (11)$$

Where: F is the value of some structural characteristic of PE-LD density, S is ethylene entropy, $a, b, c \dots$ are coefficients of the equations, $\exp = 2,7183\dots$

RESULTS OF EXPERIMENTAL DATA ELABORATION

The following criteria were used to chose the most suitable equation that fits with the data:

- correlation coefficient should be close to 1
- standard error should be as low as possible

The results of the experimental data elaboration using our computer program are presented in Table I and in Figs. 2–8.

TABLE I. Effects of ethylene entropy under the polymerization conditions on the structure and density of PE-LD

Structural characteristics	Mathematical expression	Number of points	Standard error	Correlation coefficient
Short chain branches	$\text{CH}_3/1000 \text{ C} = \exp^{(6.825 S - 4.857)}$	93	2.67	0.954
Ethyl branches	$\text{Et}/1000 \text{ C} = 3.176 + 0.0074 S^{32.56}$	13	0.94	0.981
Butyl branches	$\text{Bu}/1000 \text{ C} = 37.549 S - 34$	19	1.00	0.959
Amyl and long branches	$(\text{Am} + \text{Longs})/1000 \text{ C} = 32.926 S - 30.7$	18	1.04	0.941
Vinylidene groups	$\text{CH}_2=\text{C}/1000 \text{ C} = 0.042 + 0.01 S^{20.76}$	32	0.02	0.984
Transvinylidene groups	$-\text{CH}=\text{CH}-/1000 \text{ C} = 0.009 - 0.0013 S^{20.73}$	7	0.03	0.954
Density	$d(\text{kg/m}^3) = 1030.7 - 100.18 S$	102	3.12	0.953

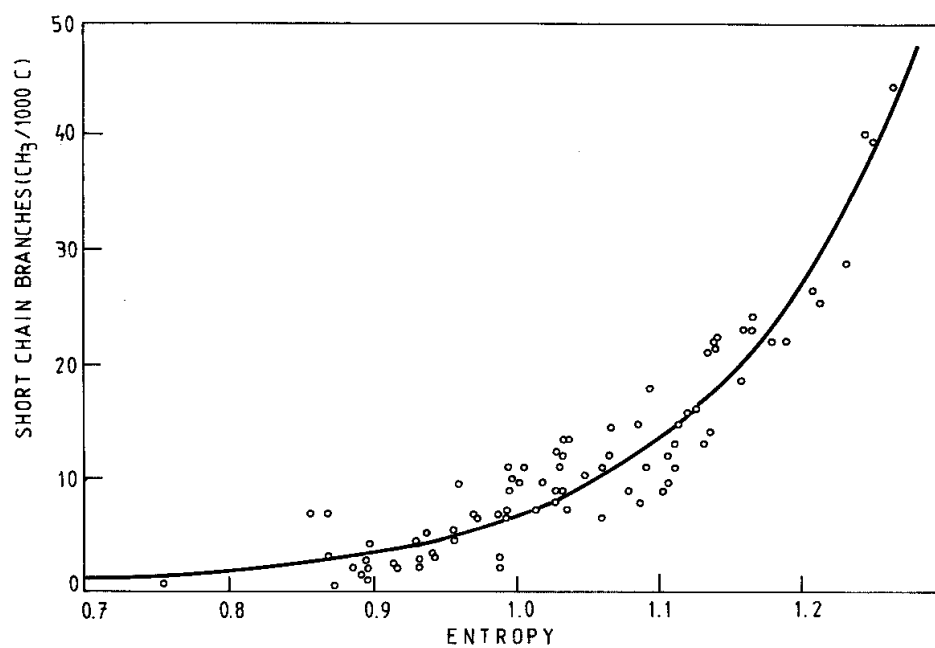


Fig. 2. The effect of ethylene entropy of short chain branches.

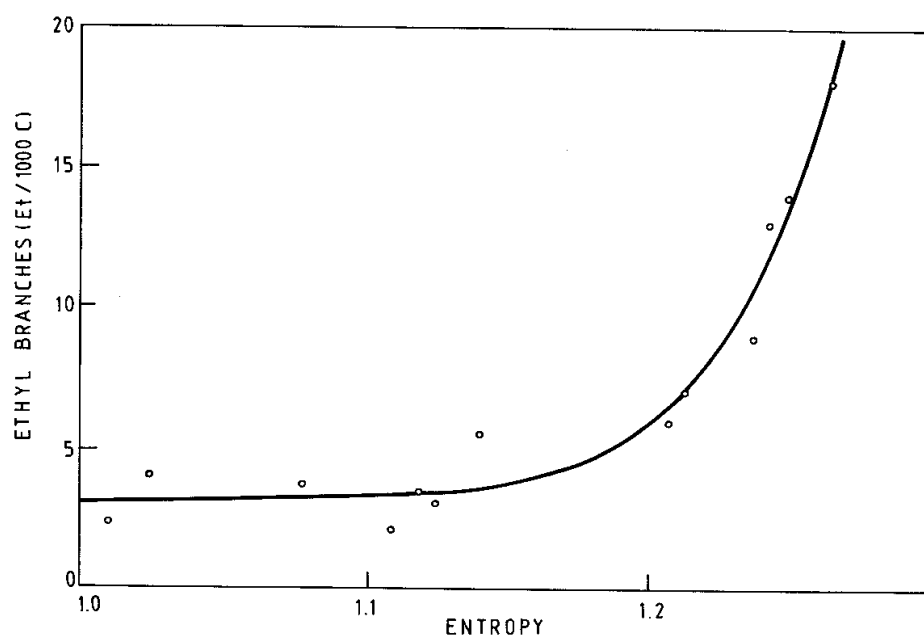


Fig. 3. The effect of ethylene entropy on ethyl branches.

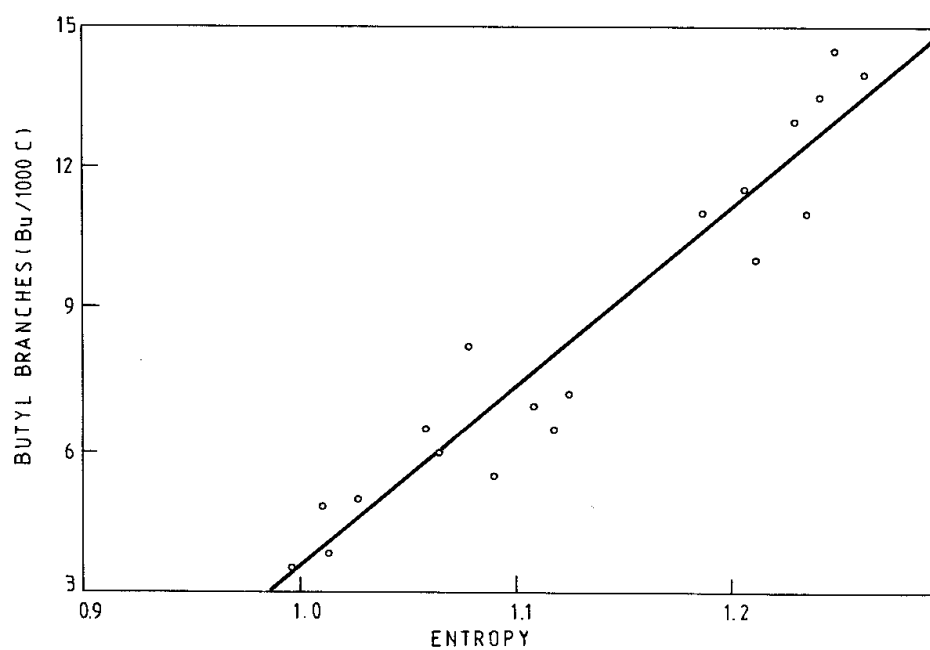


Fig. 4. The effect of ethylene entropy on butyl branches.

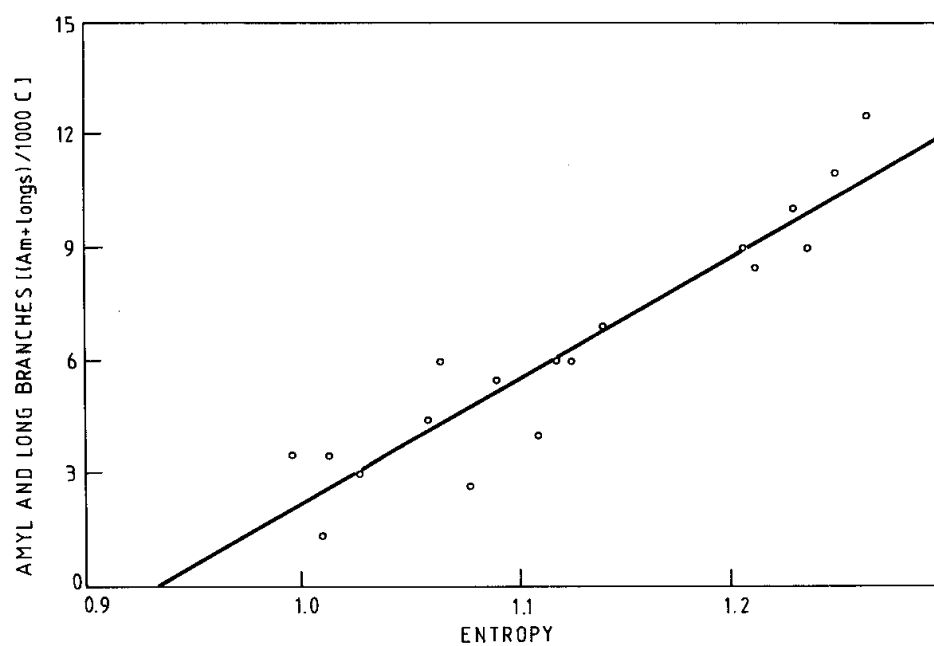


Fig. 5. The effect of ethylene entropy on amyl and long branches.

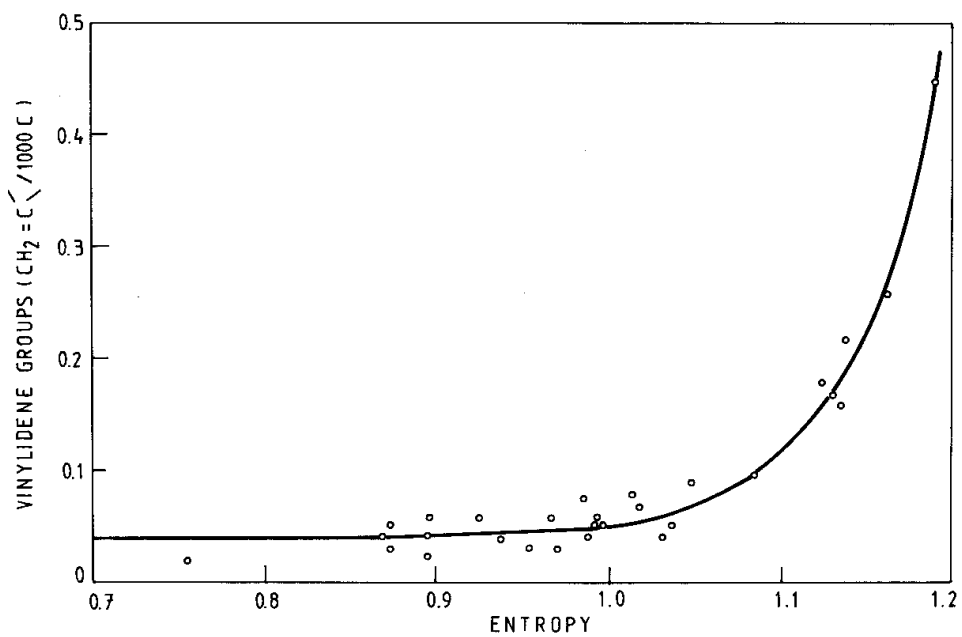


Fig. 6. The effect of ethylene entropy on vinylidene groups.

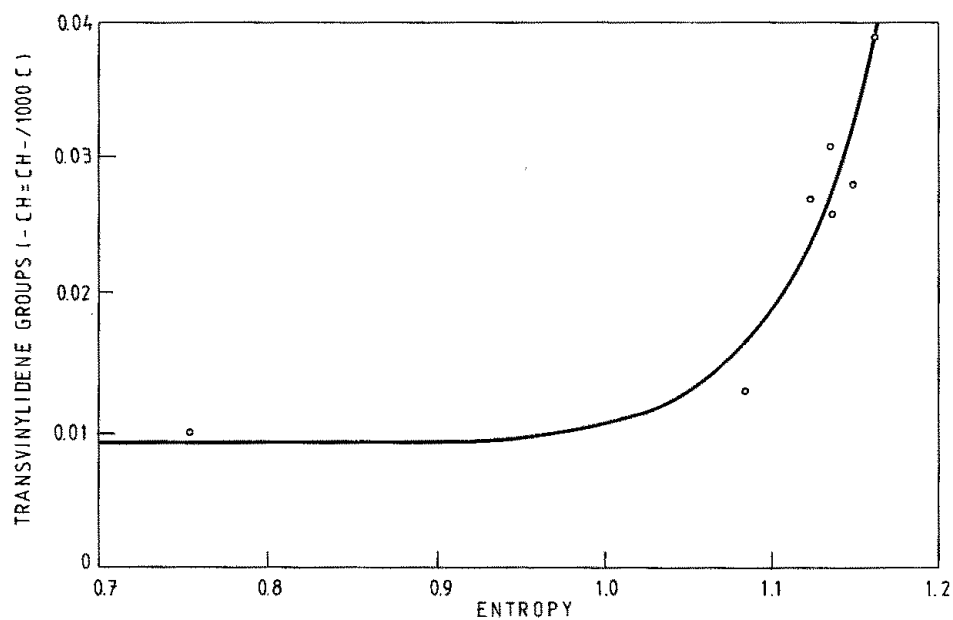


Fig. 7. The effect of ethylene entropy on transvinylidene groups.

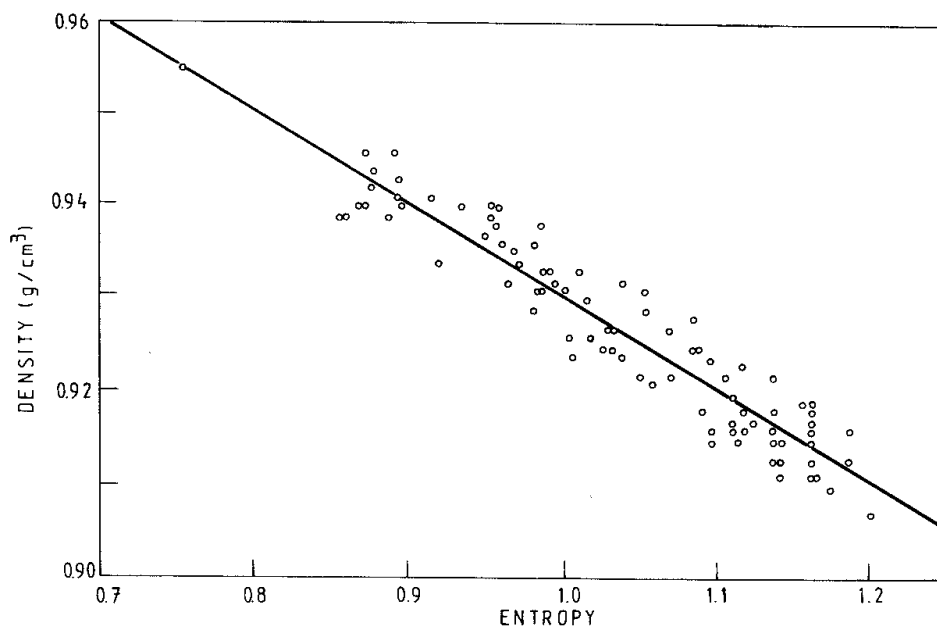


Fig. 8. The effect of ethylene entropy of PE-LD density.

CONCLUSION

A computer program was developed that enables the better manipulation of experimental data. Using the computer program, mathematical relations between ethylene entropy and structural parameters and density of PE-LD were established. The mathematical relations concerning the effects of ethylene entropy on the short and long chain branches, the vinylidene and transvinylidene groups and the density of PE-LD are in very good agreement with the experimental data.

Acknowledgement: This paper is dedicated to Nebojša Mitričević and Petar Savić, PE-LD plant engineer and supervisor.

ИЗВОД

ЗАВИСНОСТ СТРУКТУРНИХ ПАРАМЕТАРА И СВОЈСТВА ПОЛИЕТИЛЕНА НИСКЕ ГУСТИНЕ ОД УСЛОВА СИНТЕЗЕ

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Структура макромолекула полиетилена ниске густине (ПЕНГ-а), који се добија радикалном полимеризацијом етилена под високим притисцима, је веома сложена. У ланац полимера могу бити уграђене кратке (етил, бутил и амил) и дуге бочне гране, као и незасићене везе (винилиденска и трансовинилиденска). Те структурне карактеристике

знатно утичу на својства ПЕНГ-а: густину и брзину течења растопа полимера. Густина и брзина течења растопа (обрнуто пропорционална молској маси полимера) значајно утичу на прераду и примену ПЕНГ-а. У претходним истраживањима у нашој лабораторији развијен је математички модел за предсказивање структуре и својстава ПЕНГ-а у зависности од услова полимеризације. Тај модел показао је неке недостатке. Циљ овог рада био је да се ти недостаци превазиђу и да се омогући боља манипулација експерименталним подацима користећи компјутер. Направљен је компјутерски програм помоћу којег су успостављени математички односи између ентропије етилена и структурних параметара и густине ПЕНГ-а. Сви доступни експериментални подаци (више од 300 тачака) су обрађени на компјутеру. Исти се могу добро описати математичким релацијама о утицају ентропије етилена на садржај кратких и дугих бочних грана, винилиденских и трансвинилиденских веза, као и на густину ПЕНГ-а.

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