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Compression, supramolecular organization and free radical polymerization of ethylene gas

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ABSTRACT

At low pressure, ethylene gas consists of single translating and rotating molecules and behaves as an ideal gas. With decrease of free volume by compression, various rotating supramolecular particles are formed, which require less space for the movement: molecular pairs, bimolecules and oligomolecules. The appearance of a new kind of particles is manifested as a phase transition of the second or third order. An ideal gas consists of single translating and rotating molecules. α phase consists of rotating single molecules and rotating molecular pairs and it exists when the volume V is reduced to $V_c < V < 2V_c$. (V_c is critical volume). β phase consists of molecular pairs and bimolecules and it exists when $V < V_c$ and $S > S_c$. (S_c is critical entropy). γ phase and liquid ethylene consist of bimolecules and oligomolecules and they exist when $S < S_c$. The main goal of this article is to publish how we developed that model and what were thermodynamical, physical and chemical evidences which confirmed its validity. Instead of the classical theory of radical polymerization, we applied Kargin and Kabanov theory of polymerization of organized monomer to interpret high pressure free radical polymerization of ethylene. The arrangement of monomer molecules in individual supramolecular particles and the supramolecular organization of whole system have decisive effects on the mechanism and kinetics of polymerization and on the formation of polymer structure and properties, i.e. molecular mass and its distribution, branching, density, etc. There is isentropic rule: the same structures and properties are obtained for polyethylene if the entropy of ethylene under polymerization conditions is the same, regardless the differences in other polymerization conditions, i.e. reactor type, pressure, temperature and method of initiation. Mathematical models of the effect of ethylene entropy on polyethylene structure and density enable practical design of polyethylene with desired characteristics. Finally, it is mentioned that we expanded the model of ethylene to other gases and liquids as well as to other polymerization cases, including liquid monomers and olefins polymerization by Ziegler-Natta, metallocene and Phillips catalysts. **Polyolefins J (2019) 6: 23-41**

Keywords: Ethylene gas compression; ethylene supramolecular organization; ethylene supercritical phase state; ethylene free radical polymerization; low density polyethylene; polyethylene structure.

CONTENT

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INTRODUCTION

It was discovered in 1933 that ethylene can be polymerized by free radicals [1]. According to the generally accepted theory of free radical polymerization it is believed that in each propagation step one by one ethylene molecule M is connected to growing macroradical $R_n^\bullet$ producing one by one repeating unit (Eq. 1). It is believed that the polymerization mechanism and kinetics and the structure of macromolecular chain are determined mainly by the interaction of active center (R$^\bullet$) and an individual monomer molecule M. Consequently, the approach and the addition of each monomer molecule to an active center is considered as an independent event, i.e. the surrounding molecules do not participate in the event and cannot affect it.

$$R_n^\bullet + CH_2=CH_2 \rightarrow R_n-CH_2-CH_2^\bullet; \text{ i.e. } R_n^\bullet + M \rightarrow R_{n+1}^\bullet \qquad (1)$$

This very simple chemical reaction, however, can be performed only if ethylene gas is compressed to very high pressure, from 10 up to 700 MPa. Immediately after this discovery, a crucial question was raised: why such high pressure was needed? Hunter [2] noticed that the density of compressed ethylene gas at the polymerization conditions (100-300 MPa, 420-570 K) in industrial plants was 0.40-0.50 g/cm^3 (i.e. its molar volume was 50-70 cm^3/mol). This value exceeds the density of the randomly packed ethylene molecules which is 0.28 g/cm^3 (100 cm^3/mol). Hunter calculated that the average distance between the molecules under polymerization conditions was 0.4-0.5 nm, which was less than the diameter of molecule (0.56 nm). He concluded that ethylene molecules in these conditions were regularly packed, suitably oriented and distorted. According to Hunter, the compression contributes to certain organization of ethylene molecules, which is a prerequisite for successful polymerization. However, he did not explain how the molecules are packed, oriented and distorted.

Hence, in MSc (1978) and PhD (1981) [3,4] theses, we explained the self-assembling, orientation and deformation of ethylene molecules and developed a model of physicochemical and phase state of compressed ethylene in supercritical conditions

(Figure 12). We applied this model to explain the free radical polymerization of ethylene and published many of articles in journals and scientific conference proceedings. Many details of mechanism and kinetics of free radical polymerization of compressed ethylene and macromolecular structure formation have been thoroughly elaborated. The importance of phase states and supramolecular species for the industrial production of low density polyethylene (PELD) was elaborated and verified in several production plants.

Although presented in MSc and PhD theses, however, we have never published how we developed that model (Figure 12) and what were thermodynamical, physical and chemical evidences which confirmed its validity. It is the aim of this article to explain how and why various supramolecular species are formed and what phase transitions occur by ethylene gas compression. The explanation is almost the same as that given in PhD thesis.

The conditions of a) solid-liquid, b) solid-gas and c) liquid-solid phase transitions of some substances can be presented by the relevant curves in pressure-temperature diagram (Figure 1).
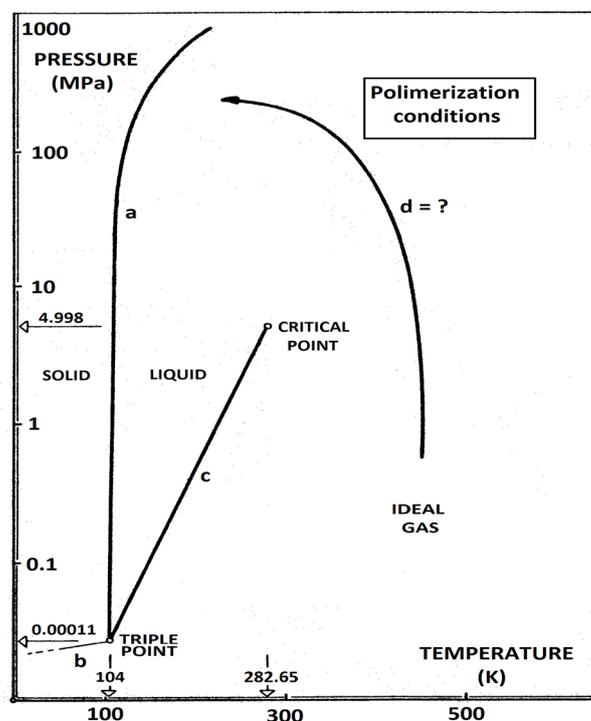
Figure 1. Pressure-temperature diagram for ethylene, drawn according to data [1,5]. Critical point: T_c=282.65 K, P_c=5.06 MPa, V_c=127.64 cm^3/mol; Triple point: T_t =104 K, P_t=111.5 Pa, V_t=39.08 cm^3/mol.
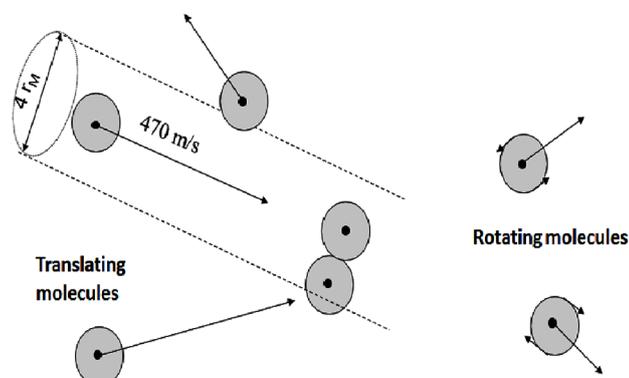
While the phase transitions denoted by curves a, b and c have been thoroughly examined, relatively less is known about the transition from ideal gas to liquid state above the critical point along the path denoted by line d. It is said [6] that there exists a gradual transition from gas to liquid (without condensation) and that a system is homogenous all the time along the path d.

Since this supercritical region of the ethylene gas has great importance for the production of low density polyethylene (PELD) by free radical mechanism, we considered thoroughly the ethylene compression from ideal gas state up to the very high pressure.

FORMATION OF ROTATING MOLECULES AND MOLECULAR PAIRS

At low pressures and high temperatures, ethylene behaves as an ideal gas. Molecules move in a chaotic manner, in all directions. A molecule translates freely if there is no other molecule at distance less than 2 r_M from its path, where r_M is radius of a molecule (Figure 2). In ideal gas, however, the molecular collisions of ethylene are frequent: there are $\approx 10^{23}$ molecular collisions in one cubic centimeter per second, i.e. each ethylene molecule collides with other molecules $\approx 8 \times 10^9$ times per second. Due to collision, a part of the kinetic energy of translation is transformed into the rotational energy and intramolecular vibrations [6] (Figure 2).

The volume of ethylene is reduced by compression, molecules come closer to each other and the translating molecules collide more frequently. As a result of this state of collision, more and more molecules turn into the rotational and vibrational modes of movements which need less space than translation.

At some low volume V_M, the free space for translation of molecules is completely exhausted, the ethylene gas contains mainly the free rotating single molecules. According to L. Onsager [7], the space occupied by a rotating particle is determined as the space in which the center of some other particles cannot be located. For a spherical particle, the occupied volume is equal to the sphere having a radius equal to the diameter of particle itself, i.e. the volume of occupied sphere is four times the volume of spherical particle itself. Hence, free rotation of compressed ethylene is possible if the average distance between the molecules exceeds the diameter of the molecules (2 r_M in Figure 3a), i.e. until the molar volume of gas exceeds V_M calculated by Eq. 2. It follows from Eq. 2 that the molar volume necessary for free rotation of molecules is V_M = 222 cm³/mol $\cong$ 0.008 m³/kg.
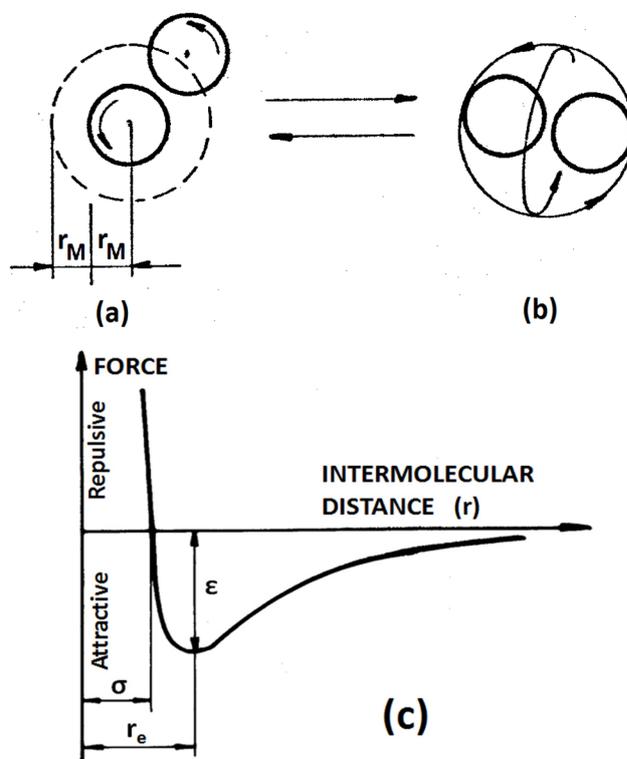
Figure 3. (a) Restriction of free rotation of single molecules; (b) Formation of molecular pair; (c) General shape of Lennard-Jones's potential [8]. For ethylene: s = 0.4163 nm and r_e = 0.466 nm [9].

Figure 2. Restriction of free translation and formation of rotating single molecules by collision of two translating molecules.

$$V_M = (2/3) \ (2r_M)^3 \ \pi \ N \qquad (2)$$

Here, V_M is the molar volume of free rotating ethylene molecule, $r_M = 0.28$ nm is the radius of molecule, and N is Avogadro's number (N=6.022× 10^{23} molecules/mol).

Once ethylene gas is compressed to volume $V_M = 222$ cm³/mol the whole space is occupied by single free rotating molecules. The value of V_M, however, is 3-4 times higher than the volume at polymerization conditions, i.e. 50-70 cm³/mol.

When ethylene gas is further compressed to the volume less than V_M, the molecules are forced to organize and coordinate their mutual movements, so the rotating molecular pairs are formed (Figure 3b). The individual rotation of two single molecules is transformed to cooperative rotation of two paired molecules. We assume that two ethylene molecules are at the distance r_e that corresponds to the minimum potential energy according to Lennard-Jones's model (Figure 3c). The experimental values for ethylene molecules, based on the viscosity data, are $\sigma = 0.4163$ nm and $r_e = 0.466$ nm [9].

The tendency toward the formation of a molecular pair can be explained by the quadrupole moment in the ethylene molecule [10]. Each bond C-H is partially polarized with a positive charge on the hydrogen atom and a negative charge on the carbon atom: dipole moment is 1.05 Debye (3.5× 10^{-30} Cm) [11]. Two ethylene molecules can be mutually oriented in twelve configurations [14]. The quantum-mechanical

calculations of intermolecular forces were carried out for the parallel and the perpendicular configurations of ethylene [14-16]. We suggest a crosswise configuration for the molecular pair (Figure 4) because it enables a very dense packing of molecules and a maximum overlapping of the positive charged hydrogen atoms from one molecule with the negative charges of electrons in π bonds of the neighboring molecule. Such configuration should be very stable in the case of ethylene molecules [17] as well as for the molecules of some other substances [18].

The molar volume of a sphere occupied by rotating of a molecular pair (V_p), whereby the radius of the sphere is equal to the equilibrium parameter re for Lennard-Jones's model, can be calculated from Eq. 3. By the experimental value of $r_e = 0.466$ nm [9], it follows that $V_p = 127.7$ cm³/mol.

$$V_p = (2/3) \ (r_e)^3 \ \pi \ N \qquad (3)$$

It should be noticed that due to cooperative motion, a rotating pair of molecules needs almost two times less space than the rotation of two individual molecules; i.e. $V_p = 127.7$ cm³/mol versus $V_M = 222$ cm³/mol. It means that the coupling of two molecules in a pair liberates a huge space (≈ 100 cm³/mol). This is in accordance with Le Chatelier-Braun's principle: if some external action is applied on the system in equilibrium, the equilibrium is shifted in the direction in which the system has a tendency to suppress to external action and to restore its previous state. In the case of compression as an external action, the free volume of the system is reduced, but the system is shifted to create free space by transformation of molecular motions to such kinds that need less space: from the translation to the rotation of individual molecules, and then to cooperative rotation of two paired molecules.

It can be expected that with the further pressure increase, the volume of ethylene gas is reduced from 222 to 127.7 cm³/mol. Meanwhile, portion of the rotating molecular pairs will grow over the portion of the single rotating molecules. Once the volume 127.7 cm³/mol is achieved by compression, almost all molecules should be coupled in rotating pairs with negligible space between the pairs.
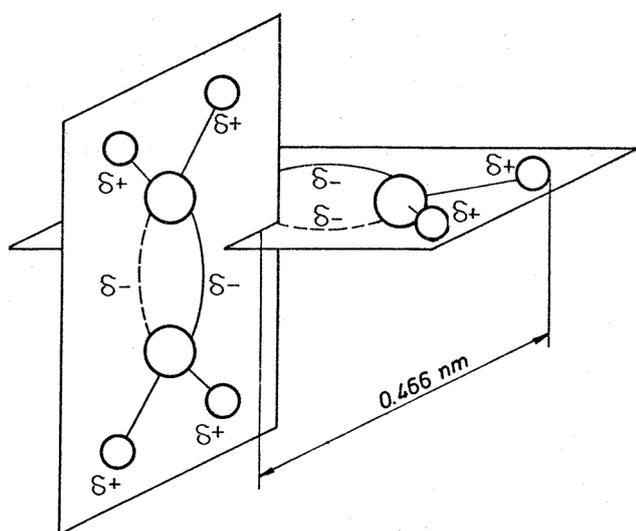

Figure 4. Configuration of a molecular pair [3,4,12,13].

It is important to note that the volume of the molecular pair V_p (127.7 cm³/mol) is equal to the critical volume of ethylene, i.e. V_c = 127.64 cm³/mol (Figure 1). Consequently, it can be expected that at P-T conditions corresponding to the critical isochore (V = V_c = 127.64 cm³/mol or reduced volume v = V/V_c=1), the compressed ethylene gas consists almost entirely of the rotating molecular pairs with negligible space between pairs.

FORMATION OF BIMOLECULES

Molar volume of ethylene at the critical isochore (127.64 cm³/mol) is approximately two times higher than ethylene volume at commercial polymerization conditions and three times higher than a minimum volume (V_{min} = 38 cm³/mol) obtained by compression of ethylene gas at 298 K [19]. Since there is a negligible space left between different pairs, the further compression is possible on the account of space left between the molecules inside the pairs. It means that the molecules in a pair are forced to come at a distance significantly less than r_e = 0.466 nm and even less than so called "hard sphere" distance, i.e. σ = 0.4163 nm (Figure 3c).

Therefore, we assumed that instead of Lennard-Jones's potential (Figure 3c) which considers the molecules as hard spheres, it is more appropriate (and hence more correct) to apply curve (Figure 5), proposed by Roger Boscovich (1711-1787), which enables to consider molecules as soft bodies. Already paired molecules come more closely towards each other, thus forming a rotating bimolecule. A particle similar to a bimolecule is used for the interpretation
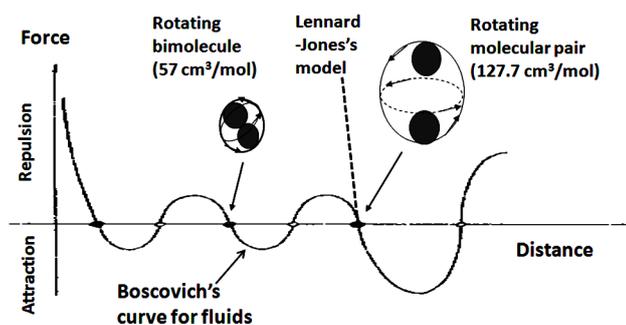
of the physical meaning of van der Waals's constant "b" (co-volume) in the well-known equation of state [10]. The co-volume b represents a half volume of a sphere occupied by two rotating molecules that touch each other. We propose that such particles really exist in compressed ethylene. Therefore, we propose that a rotating bimolecule occupies volume b = 57.1 cm³/mol, which is the empirically determined value of co-volume for ethylene [10].

Knowing the value of co-volume, a radius of a sphere necessary for the rotation of a bimolecule can be calculated as r_b = 0.356 nm. We suppose that the two ethylene molecules in such sphere are crosswise arranged (Figure 6). Such configuration of a bimolecule results from the configuration of a molecular pair (Figure 4).

FORMATION OF OLIGOMOLECULES AND THEIR BUNDLES

As pressure increases, the volume of ethylene gas decreases below the value of critical volume 127.64 cm³/mol, and the more molecular pairs are transformed to bimolecules. At some high pressure there mainly bimolecules are present and the volume of gas attains
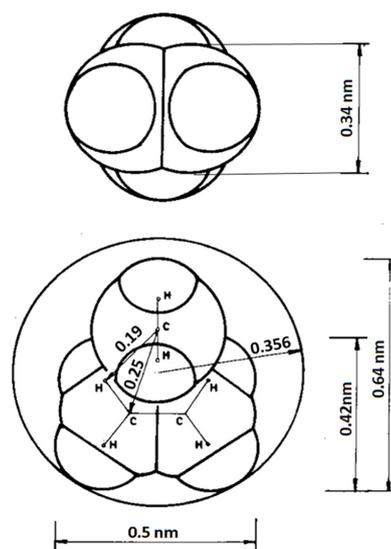

Figure 5. Roger Boscovich's curve for fluids [20-23].

Figure 6. Configuration of rotating bimolecule in two projections [4].

the value of the volume of these bimolecules, i.e. b = 57.1 cm³/mol. This volume corresponds to the volume of ethylene at the polymerization conditions, but it is still much higher than the minimum volume that can be obtained by compression of ethylene gas (V_{min} = 38 cm³/mol) [19]. Hence, further volume decrease of compressed ethylene should be possible and it can be achieved by cooling the compressed gas.

The compression of ethylene in industrial plants is performed in several steps of pressure increase, which are adiabatic in the most cases. In each step, ethylene becomes hot due to compression and it is cooled before it is subjected to the subsequent step of compression.

The bimolecules have three degree of freedom for rotation, i.e. they rotate around all three axes (Figure 7a). By cooling, they lose the rotational energy thus reducing the degree of freedom to one, which enables
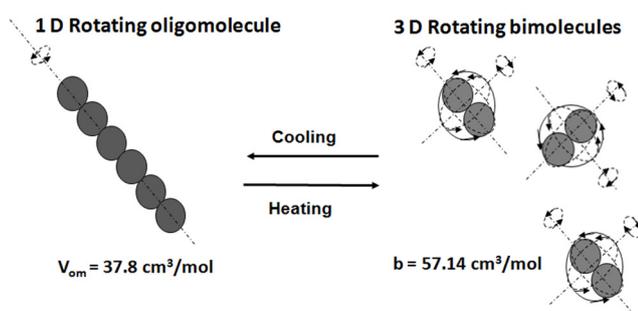

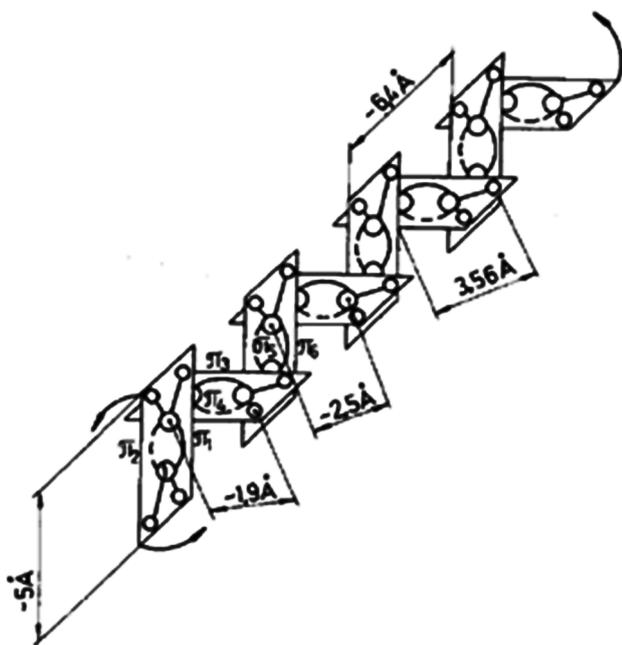**Figure 7a**. Oligomolecule formation.

Figure 7b. Configuration of a segment of an rotating oligomolecule [3,4,12] (1 Å = 0.1 nm).

the bimolecules to aggregate. Oligomolecules are formed with two and more coupled bimolecules. The configuration (Figure 7b) and the rotation of the oligomolecules around the longitudinal axis are the consequence of configuration and rotation of the bimolecules before coupling. If we accept that the length of a bimolecule coupled in an oligomolecules is nearly equal to that in the free bimolecule, i.e. L_{om} = 0.64 nm and the radius of rotation of oligomolecules r_{om} = 0.25 nm (Figures 6 and 7), the cylindrical space necessary for the rotation of an oligomolecule can be calculated by Eq. 4.

$$V_{om} = 0.5 \, r_{om}^2 \, \pi \, L_{om} \, N = 37.8 \text{ cm}^3/\text{mol} \qquad (4)$$

A further increase of pressure and decrease of temperature move the equilibrium between bimolecules and oligomolecules: the number and the length of the oligomolecules increase. Therefore, the structure of the highly compressed ethylene gas could be present with a great number of the parallel arranged rotating oligomolecules having molar volume 37.8 cm³/mol. This is in good agreement with a minimum volume (38 cm³/mol) obtained by the compression of ethylene gas at 298 K [19].

We believe that the further decrease of volume can be obtained only by the aggregation of the oligomolecule by cooling. The rotating oligomolecular bundles would be formed. This is a new step, however, toward freezing of ethylene gas noticed at 1900 MPa and 298 K [24].

PHASE STATE OF COMPRESSED ETHYLENE GAS

A gradual change from some arrangement of molecules to another one, followed by a change of disorder to order, corresponds to the phase transitions of second and higher order [25]. According to Ehrnphest's classification, a phase transition has nth order if the nth differential of Gibbs's function has a discontinuity, but (n-1)th differential has a continuity (Table 1).

Higher order phase transitions are characterized also by the changes in the magnetic and electric properties

Table 1. Classification of the phase transitions according to Ehrnphest [25].

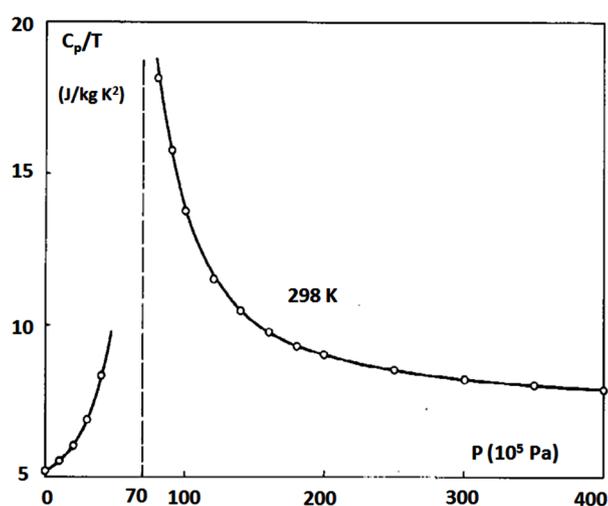| Order of phase transition	Change of properties	
	Continuously	**discontinuously**
I order	G	$S = -(dG/dT)_P$; $V = -(dG/dP)_T$
II order	S, V	$d^2G/dT^2 = -(dS/dT)_P = -C_p/T$ $d^2G/dTdP = (dV/dT)_P = \alpha$ (thermal expansion coefficient) $d^2G/dP^2 = (dV/dP)_T = \beta$ (isothermal compressibility)
III	C_p/T; α; β	$d^3G/dT^3 = d(C_p/T)/dT$; etc.

G-Gibbs free energy, S-entropy, T-temperature, V-volume, P-pressure, C_p-heat capacity at constant pressure.

(superconductivity), orderliness and symmetry of system. The second order phase transitions are very often denoted as "lambda transitions" because the shape of C_p curve resembles the Greek letter lambda (λ).

The proposed gradual formation of different supramolecular species in compressed ethylene gas corresponds to the phase transitions of the second and higher order. The following transitions can be expected:

a) Single rotating molecules ↔ molecular pairs at P-T conditions when the volume of compressed ethylene is 222 cm³/mol.

b) Molecular pairs ↔ bimolecules at the critical isochore, i.e. at P-T conditions when volume of ethylene V is equal to critical volume $V = V_c = 127.6$ cm³/mol = 4.56 m³/kg (or reduced volume $v = V/V_c = 1$.)

c) Bimolecules ↔ Oligomolecules; the phase transition conditions should be determined.

d) Oligomolecules ↔ Bundles, i.e. the transition to solid phase.

In this section we shall prove that the transitions (a) and (b) occur at the above mentioned conditions and find the conditions for the phase transition (c).

The effect of pressure (at 298 K) on C_p/T has a lambda shape with the discontinuance at about 7 MPa (Figure 8). At these conditions (7 MPa and 298 K) the volume is equal to critical volume, according to enthalpy pressure diagram for ethylene [26].
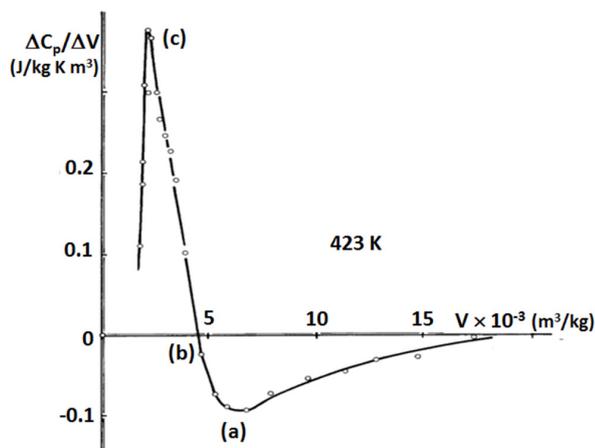
At higher temperatures, the C_p/T curves have no lambda shape, but the maxima (b) corresponding to critical volume (Figure 9). According to Wunderlich and Baur [27], such shape of the curve is characteristic of system containing particles distributed at different

Figure 8. Effect of pressure on C_p/T at 298 K [12]. Drawn according to tabulated data in [5].
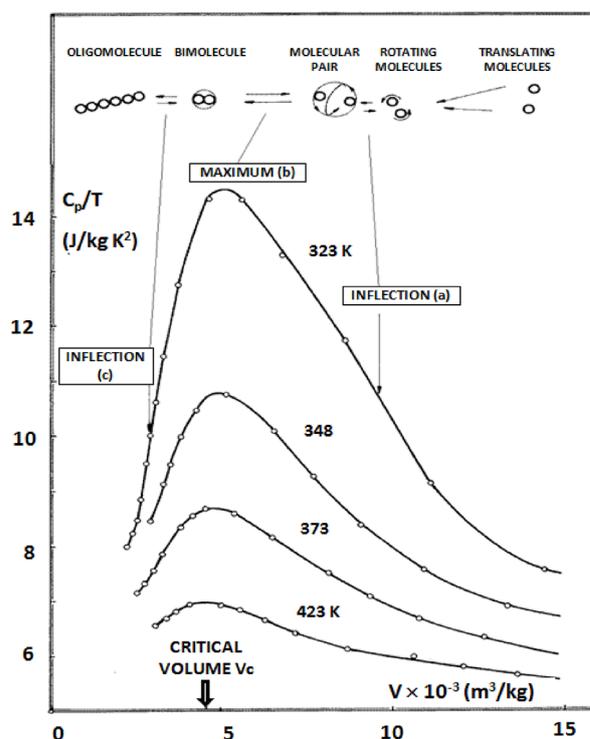
Figure 9. Effect of volume (V) on C_p/T at different temperatures, drawn according to data [5]. Inflection (a), maximum (b) and inflection (c) are denoted on the curves as well as corresponding phase transitions of compressed ethylene gas.
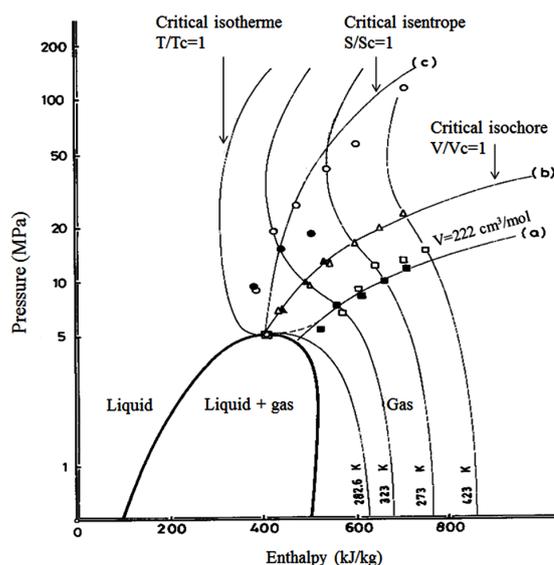
energy levels, whereby the particles of one kind transform to another kind. According to our proposal, the maxima (b) of curves in Figure 9 correspond to the onset of transformation of molecular pairs into bimolecules.

In addition to the maxima (b), the curves in Figure 9 have two inflection points: (a) and (c). We suppose that these inflection points are due to the existence of different supramolecular species in compressed ethylene. As stated by Wunderlich and Baur [27], at the points of inflections the prevailing effect of one kind of species is starting to be suppressed by the appearance of another kind. The thermodynamic meaning of these inflections, (a) and (c), is that they represent transitions of higher order than the phase transition denoted by (b).

The exact P, V and T coordinates of these inflection points can be determined by numerical differentiation of data [5] for curves in Figure 9. One example is given in Figure 10. The same procedure was applied for other temperatures. The coordinates of the inflection points (a) and (c) and the maxima (b) are drawn onto enthalpy-pressure diagram [26] as presented in Figure. 11. It is evident that the inflection points (a) are situated near isochore V=222 cm^3/mol and maxima (b) near critical isochore V/V$_c$=1, respectively, as it was predicted previously. The P, V and T coordinates of inflection points (c) are close to the critical isentrope line, i.e. at P-T conditions where the ethylene entropy is equal to the critical entropy (i.e. reduced entropy S/S$_c$ = 1).


Figure 11. Positions of the maxima (triangles) and the inflection points (circles and squares) on C$_p$ (open symbols) and C$_v$ (filled symbols) curves drawn onto enthalpy-pressure diagram [26] of ethylene.

By analyzing the data [5] of the relation between C$_v$ and V, the points of discontinuity were found and their positions were also presented in Figure 11.

Consequently, a model of the phase state of compressed ethylene gas is presented in Figure 12. There are several phases. At low pressure in ideal gas the single translating and rotating molecules exist, the

Figure 10. ΔC$_p$/ΔV versus volume of ethylene gas at 423 K, drawn according to numerical differentiation of tabulated data [5]. The values of volumes at inflection points (a) and (c) and maximum (b) in Figure 9 can be estimated.
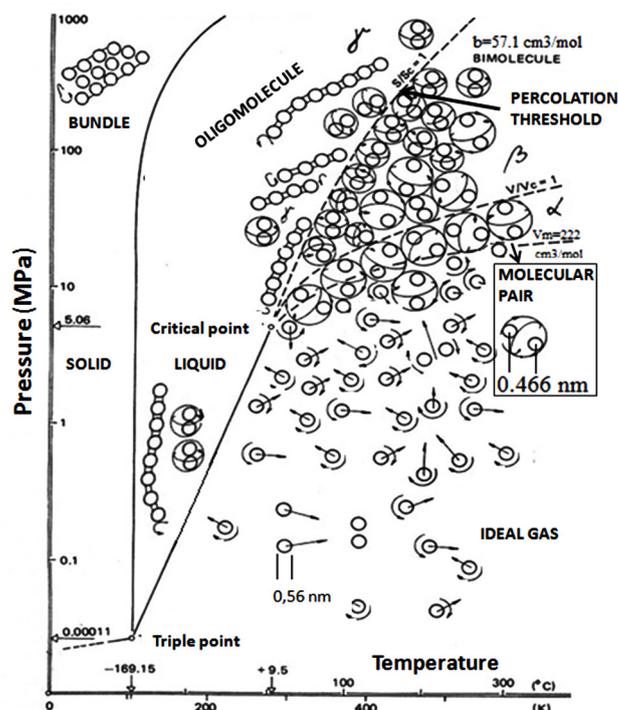
Figure 12. Model of phase state of compressed ethylene gas [3,4,12,13,28-30].

later dominating when the volume is reduced to 222 cm³/mol. At higher pressures, when volume is reduced below 222 cm³/mol, molecular pairs start to be formed – a new α phase appears, that consists of a mixture of the rotating single molecules and molecular pairs. Further compression contributes to molecular pairs prevailing over rotating single molecules. At the condition near critical isochore, molecular pairs mostly exist. At higher pressure, above critical isochore ($V/V_c = 1$) the molecular pairs start to be transformed to bimolecules – a new β phase appears consisting of a mixture of molecular pairs and bimolecules. The bimolecules dominate at the conditions close to critical isentrope, i.e. $S/S_c=1$. At lower entropy, i.e. $S < S_c$, bimolecules start to be coupled in oligomolecules - a new γ phase appears consisting of a mixture of bimolecules and oligomolecules, the latter dominating at lower temperature close to solidification of ethylene.

By cooling γ ethylene below critical point a liquid phase appears which consists of a dynamic equilibrium of two micro phases, a disordered one having 3D rotating bimolecules and ordered one having 1D rotating oligomolecules. The bimolecular phase is gradually transformed to oligomolecular by further cooling and completely diminished at the solidification temperature when only oligomolecular phase exists. Hence, the empirical value for specific volume of solid phase of ethylene at triple point V_t = 39.08 cm³/mol is close to the volume of rotating oligomolecule V_{om} = 37.8 cm³/mol calculated by dimensions of its molecule. This volume corresponds to above mentioned transformation d) Oligomolecules ↔ Bundles, i.e. the transition to solid phase.

## EFFECTS OF SUPRAMOLECULAR SPECIES ON PROPERTIES OF COMPRESSED ETHYLENE GAS

The essential differences between the supramolecular species of ethylene are the number of associated molecules and the distance between them, the kind of movement and the kind and degree of deformation of molecules. The presence of the different supramolecular species should affect all physical, thermodynamic and chemical properties of ethylene. Some noticeable changes, i.e. a minimum or a maximum, an inflection or change of slope of the curves that represent the effects of pressure, temperature and volume (or density) on some property, should be found at the phase transition conditions: at V=222 cm³/mol (ideal gas to α phase transition), $V = V_c = 127.6$ cm³/mol (α-β phase transition) and $S/S_c = 1$ (β-γ phase transition).

We have analyzed a plenty of published ethylene properties data: compressibility factor (Z=PV/RT) and product PV; heat capacities at constant pressure (C_p) and constant volume (C_v); entropy (S); viscosity (η); sound velocity (a); infrared spectra (IR), molar polarization (PM) calculated by dielectric constant and molar refraction (L_r) by refractive index measurements [4]. Here, we present only data for compressibility factor and molar refraction.

Compressibility factor

The effects of pressure on compressibility factor Z = PV/RT and product PV have inflection points and minima (Figure 13) at those P-T coordinates which correspond to the proposed ideal gas to α phase and
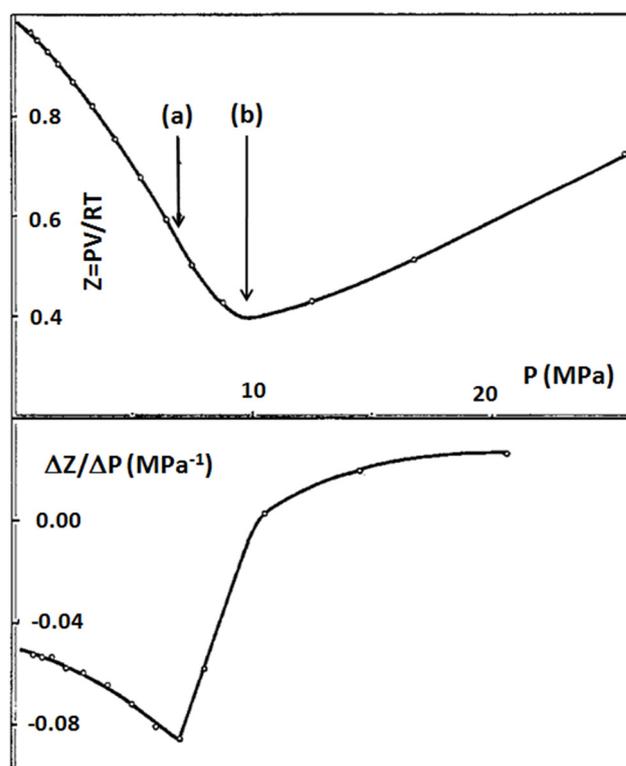
Figure 13. Effect of pressure P on the compressibility factor Z (upper) and derivation ΔZ/ΔP (bottom) at 313 K. Based on numerical data in [1,31].
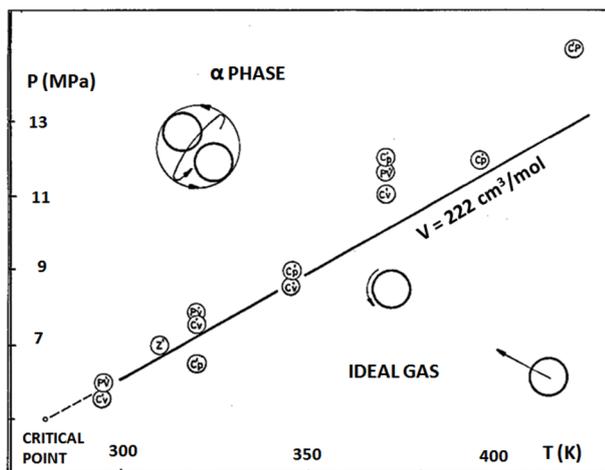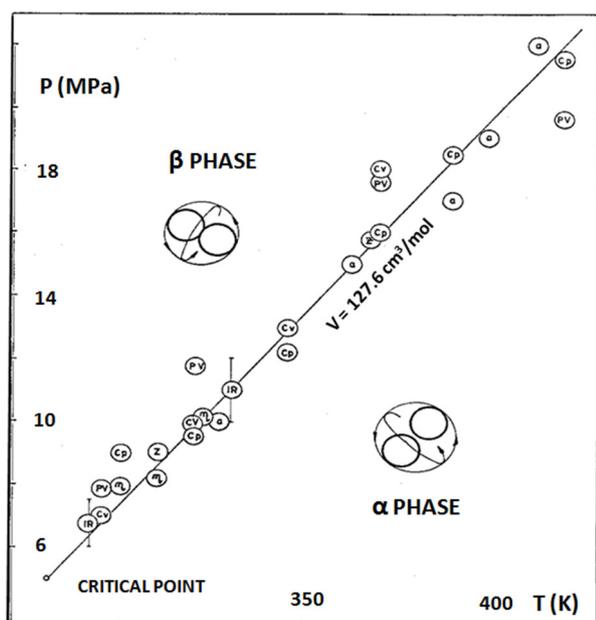
Figure 14. P-T coordinates of the marked changes of ethylene properties are situated close to predicted ideal gas to α phase transition at isochore V=222 cm³/mol [4].

α-β phase transitions (Figures 14 and 15).
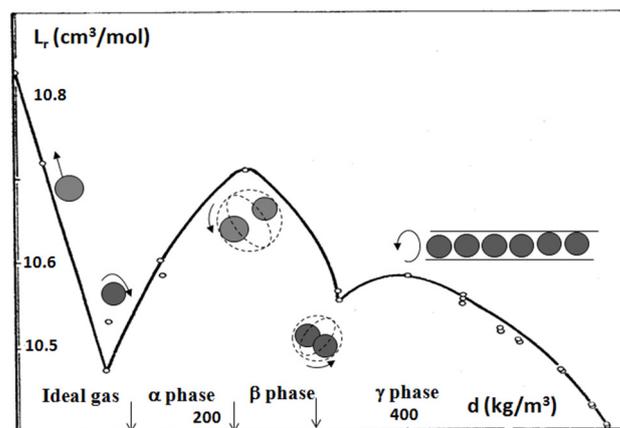
Molar refraction

Due to decrease of free volume by compression the external movement of molecules is restricted and transformed to different types of rotation that need less space. Simultaneously, a part of external movement of molecules is transformed to their internal movement, i.e. the displacement of electrons (electronic polarization) and the change of the lengths and angles of the chemical bonds (atomic polarization). Generally,

the main contribution to molar polarization due to the displacement of electrons (90-95%), but only a few percent (5-10%) due to the displacements of atoms [32]. High molar polarization means that the volume of a molecule itself is increased due to displacement of its electrons and atoms. Molar refraction can be presented by: a) Lorentz-Lorenz function, i.e. $L_r = (n^2-1)/(n^2+2)d$, where n is refractive index and d is density of a substance, i.e. compressed ethylene, and b) Clausius-Mosotti function using the data of the dielectric constants of compressed ethylene. Based on the refractive index measurements, Michels et al. [33] calculated the Lorentz-Lorenz function. We presented their data in Figure 16 and denoted the phase transition conditions and type of supramolecular species.

In ideal gas an ethylene molecule translates with a speed ≈470 m/s, and collides with other molecules very frequently (≈8× 10^9 times per second) and with very high intensity. In a cubic centimeter there are ≈10^{23} collisions per second of all the molecules. The electrons of the colliding molecules are highly excited. Consequently, L_r has a high value (at d ≈ 0 in Figure 16). Due to the collisions, the translating molecules are transformed into rotating molecules. The highest concentration of the rotating molecules is near the phase transition from ideal gas to α phase. There are no intensive collisions between them, i.e. rotating molecules only slightly push each other. The electrons in the molecules settle down. Consequently, L_r attains

Figure 15. P-T coordinates of the marked changes of ethylene properties are situated close to predicted α-β phase transition at critical isochore V = V_c = 127.6 cm³/mol [4].

Figure 16. Lorentz-Lorenz function L_r (molar refraction) as a function of ethylene density at 298 K. Maximal errors of L_r are in the range 0.015-0.040 (from Table III in [33]). We denoted the predicted phase transition conditions (↓) and type of supramolecular species.

a minimum value close to transition of ideal gas to α phase (Figure 16), where the molecular pairs start to be formed. In the crosswise configuration of ethylene molecules in a molecular pair (Figure 4), the four inner hydrogen atoms (i.e. protons) are close to π electrons of the neighboring molecule. Strong π electrons displacements have to be expected. The highest concentration of molecular pairs is at the α-β phase transition and consequently L_r attains a maximum value (Figure 16). In β phase the bimolecules start to be formed. The molecules in the bimolecules are packed more closely. The C=C bonds become extended (i.e. atomic polarization is increased), but the electrons are partially localized on carbon atoms (i.e. π electronic polarization is decreased). The highest concentration of the bimolecules is near β-γ phase transition, and consequently, L_r again attains a minimum value (Figure 16). In γ phase the oligomolecules with the stacked π bonds (Figure 7b) start to be formed. The electrons are again excited, contributing to a slight increase of L_r (γ phase in Figure 16). Formation of oligomolecular bundles at very high density contributes to decrease of L_r. It should be noticed that the described maxima and minima on L_r curve are observed close to the densities where the predicted phase transitions occur.

Similar behavior is in the case of molar polarization as determined by the Clausius-Mossoti function, i.e. a maximum on the molar polarization is at the conditions where the molecular pairs dominate, i.e. near α-β phase transition at critical isochore conditions: $V = V_c = 127.64$ cm³/mol (i.e. $C_c = 7.8$ kmole/m³) [4]. The experimental data for ethylene and other gases [34] has proved this fact.

Entropy change

The proposed formation of supramolecular particles and phase transitions contribute to drastic changes of degree of order – from the chaotic movement of molecules at low pressure up to the highly organized movement of molecules in quasi-crystalline species (oligomolecules) at high pressures. Hence, the corresponding drastic decrease of entropy is expected. Indeed, the data [26] proved such expectation (Figure 17): a drastic decrease of entropy occurs at α-β phase transition achieving very low value in γ phase.

Polymerizability of supramolecular species

The differences between supramolecular species of ethylene have decisive effects on their polymerizbility. Two ethylene molecules are more squeezed in bimolecules and oligomolecules than in a molecular pair (Figure 5 and 12). Hence, C=C bonds are extended and π electrons are partially localized on carbon atoms in the bimolecules and oligomolecules, but not in the molecular pairs. Hence, the molecular pairs are less reactive toward the free radicals. That is the reason why the free-radical polymerization of ethylene is possible only in β and γ phases in which bimolecules and oligomolecules exist, but not in ideal gas and α phases where the single molecules and molecular pairs exist (Figure 17).

Not only the deformation of molecules, but also their mutual orientation in the bimolecules and oligomolecules favors their bonding by macroradicals in the course of polymerization [2, 35]. The whole bimolecule or oligomolecule reacts at once. Hence, the generally accepted concept that in each propagation step one by one ethylene molecule M is connected to growing macroradical producing one by one repeating unit (1) is not applicable here. Instead of that, one by one bimolecule (or oligomolecule) is connected, producing one by one segment of a macromolecular chain (Eq. 5).

$$R_n{}^{\bullet} + m(CH_2=CH_2) \rightarrow R_n{-}(CH_2{-}CH_2)_{m+n}{}^{\bullet} \text{ i.e.}$$
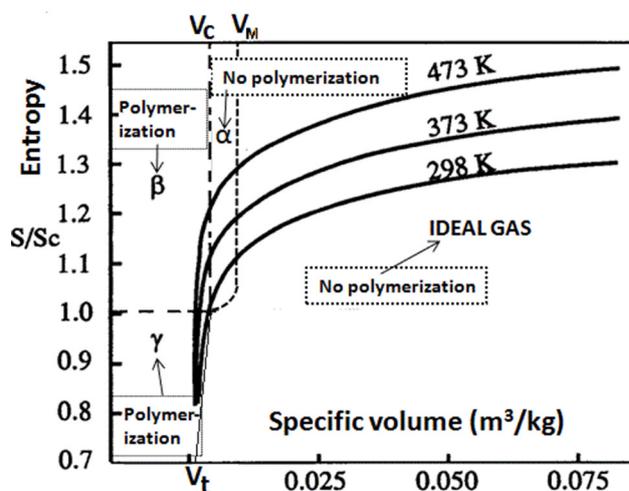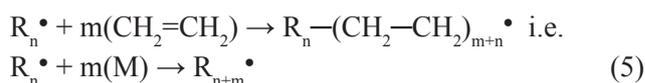$$R_n{}^{\bullet} + m(M) \rightarrow R_{n+m}{}^{\bullet} \qquad (5)$$

Figure 17. Dependence of reduced entropy on the volume of ethylene [4,13,36] based on [26]. Phase states are denoted according to Figure 12.

Here, m = 2 for bimolecules and m > 2 for oligomolecules.

This is in accordance with theory of organized monomer polymerization (TOMP) developed by Kargin and Kabanov [37]. They emphasized that there were some cases (in solid, liquid and adsorbed monomer systems) in which monomer molecules were organized and existed as clusters of *m* molecules (mM). According to TOMP, the approach and the addition of each monomer molecule to an active center are not independent events, as it is in classical interpretation (Eq. 1), since each cluster behaves as a single physical and chemical entity and the whole cluster mM is enchained at once in a single propagation step (Eq. 5). Hence, the arrangement of monomer molecules in the individual supramolecular particles m(M) as well as the supramolecular organization of the whole system have decisive effects on the mechanism and kinetics of polymerization as well as on the formation of polymer structure, i.e. molecular mass and its distribution, branching, stereo regularity, etc.

Instead of the classical theory of radical polymerization, we applied Kargin and Kabanov [37] theory to interpret high pressure free radical polymerization of ethylene [36]. In the course of polymerization, the more reactive species are continuously drawn from the system. The dynamic equilibrium between the supramolecular species of ethylene is disturbed and moved toward the formation of the missed species. The transformation of one kind of species to other ones could be the reaction rate limiting step. On this base, in each ethylene phase the theoretical values of the energy and volume of activation of polymerization were calculated and a good agreement with the experimental data was obtained [12,13,29,30,38].
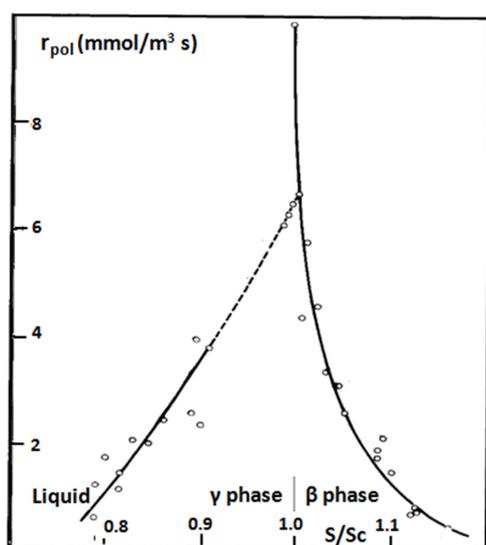
Philosophical considerations [3,4,20,21,38] were preceded by our works on ethylene polymerization about which we have published several dozen articles in journals and conference proceedings: the mechanism [12,39] and kinetics of polymerization [13,29,30], origin of polyethylene structure formation (short and long branches [28-30,39-41], unsaturated bonds [29,30,41], molecular mass [13,29,30] and its distribution [29,30]), effects of polymerization conditions on polyethylene density [29,30,41] and melting [29,30], importance of ethylene phase state for industrial process operation [42,43]. Here, we shall emphasize the main conclusions published in our articles where the details are extensively elaborated.

Table 2. Effects of ethylene phase state on the kinetics of polymerization and polyethylene structure and density [13,29,36].

Characteristics of polymerization and polyethylene structure and density	Phase state of ethylene		
	β	β-γ transition	γ
Kinetics of polymerization			
Initiation rate	High	Very high	Moderate
Induction period	No	No	Up to 5 hours
Autoacceleration	No	No	Yes
Polymerization rate	High	Maximum	Moderate
Volume of activation (cm³/mol)			
Theoretically predicted	-70	-19	-7 up to -1
Measured by experiments	-72 up to -53	-23 up to -18	-10 up to -3
Energy of activation (kJ/mol)			
Theoretically predicted	78	62	6 up to 41
Measured by experiments	58 up to 77	61 up to 69	6 up 37
Termination rate	Very high	High	Very low
Polyethylene structure and density			
Number of branches per 1000 C atoms	10-60	8-10	0-10
- Ethyl branches	0-20	0	0
- Butyl branches	5-15	3-5	0-3
- Amyl and longer branches	3-15	3	0-3
Vinylidene bonds/1000 C atoms	0.06-0.5	0.06	0-0.06
Molecular mass ($M_n \times 10^{-4}$)	1-5	2-5	5-45
Molecular mass distribution (M_w/M_n)	1-8	20-22	15-22
PE density (kg/m³)	900-930	930	930-960

Considering polymerization in β phase and γ phase there are many differences in the kinetics of polymerization and resulting polyethylene structure and properties (Table 2). As it is predicted by TOMP, polymerization in high ordered γ phase has induction period, moderate initiation and polymerization rates, autoacceleration and low termination rate.

Polymerization rate (r_{pol}) in disordered β phase deviates from classical free radical polymerization theory which predicts that r_{pol} should increase with the increase of temperature. It was noticed by experiments [44-46], however, that r_{pol} decreases with the increase of temperature in β phase. This anomaly is because in β phase at high temperature there is a low concentration of polymerizable bimolecules, which are separated by non-polymerizable molecular pairs (Figure 12). Hence, there a low polymerization rate (r_{pol}) is expected. There are more bimolecules at lower temperatures in β phase, and r_{pol} should be higher. There is inversion from discontinuous to continuous polymerizable bimolecular micro-phase at the β-γ phase transition which occurs at such pressures and temperatures at which ethylene entropy is equal to critical, i.e. $S/S_c = 1$. In percolation theory, this is so called percolation threshold. According to TOMP, there should be a maximum of r_{pol}. It was confirmed

by ethylene polymerization that the maximum of r_{pol} occurs at S/Sc =1 [44-46] (Figure 18).

(Furthermore, maximum of r_{pol} at percolation threshold occurs in free radical polymerization of liquid methyl-methacrylate [47] and in olefins polymerization by Ziegler-Natta-Kaminsky catalysts [48].)

Not only the r_{pol}, but also the other kinetic characteristics of the polymerization process (the initiation r_i, the propagation r_p and the termination r_t rates, energy of activation E_a, etc.) and the structure of polyethylene (molecular mass and its distribution, branching) are greatly influenced by supramolecular species of ethylene. The marked changes of these kinetic characteristics are near β-γ phase transition (Figure 19). This is strong chemical-kinetic evidence that this transition occurs at $S/S_c = 1$ conditions.

Isentropic rule in polymerization

Kinetics of polymerization and polyethylene structure and properties depend not only whether the polymerization conditions are in phase state is β or γ, but also how far from the β-γ phase transition (line at S/Sc=1) they are. In γ phase at very high pressure and low temperature ethylene reduced entropy can be much lower than one ($S/S_c<1$), i.e. ethylene molecules are highly organized. In β phase, at low pressures

Figure 18. Correlation of rate of polymerization (r_{pol}) with reduced entropy (S/Sc) [13,36]. Based on the data [44] on temperature and pressure under polymerization conditions we have read reduced entropy using the diagram [26] and correlated it with r_{pol}.
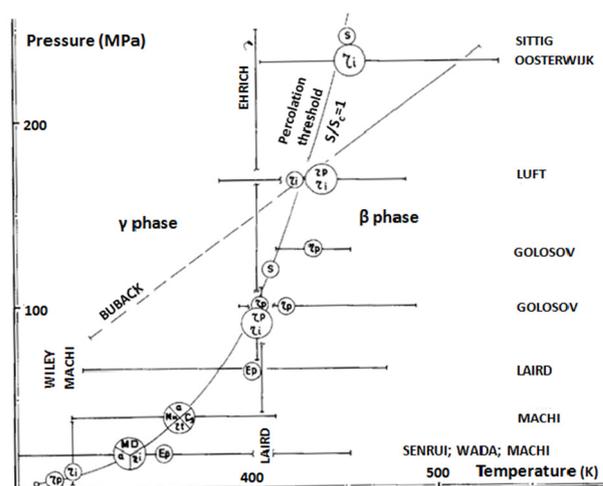

Figure 19. Marked changes of ethylene polymerization kinetics and polyethylene structural parameters were found near β-γ phase transition at S/Sc=1. Circles represent the P-T coordinates of marked changes and lines represent the range of experimental polymerization conditions for rates of initiation (r_i), polymerization (r_p) and termination (r_t), autoacceleration (a), chain transfer (C_s), molecular mass distribution (MD), activation energy of polymerization (Ep) and start-up of reaction (S). (References are in [4,13].)

Table 3. The same densities were obtained under isentropic conditions [4,29,30].

Polymerization conditions					PE density (kg/m³)	Authors
Pressure (MPa)	Temperature (K)	Entropy S/Sc	Initiation by	Reactor type		
40	333	0.950	Gamma rays	Charge	938	Machi [49]
87	353	0.940	AIBN	Charge	937	Kodama [50]
210	400	0.945	Peroxide	Autoclave	937	Mortimer [51]
430	453	0.950	Peroxide	Tubular	936	Luft [52]

and high temperature entropy is high ($S/S_c > 1$) since ethylene molecules are highly disorganized. It can be seen on thermodynamic diagram [26] that equal value of entropy can be on very different pressure - temperature combinations, e.g. first three columns in Table 3. In spite of very different polymerization conditions concerning pressure, temperature, method of initiation and reactor type, almost an equal PE density is obtained because it was equal to ethylene entropy at these pressure-temperature conditions.
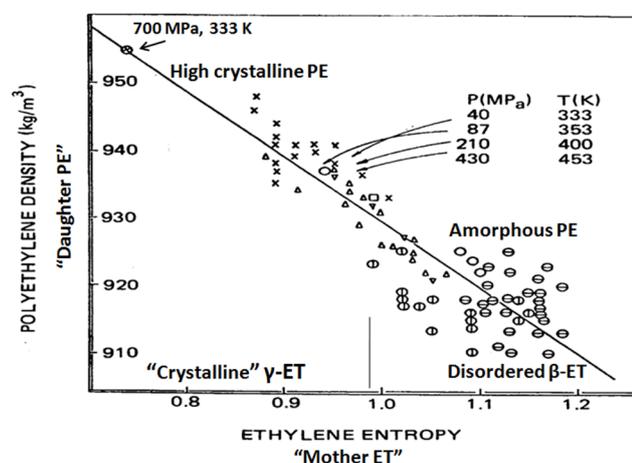
Hence, not pressure and temperature, but ethylene entropy is more convenient to present polymerization conditions. In that case, all published experimental data obtained worldwide at 40-700 MPa and 333-550 K fit one common line (Figure 20). These four runs from Table 3 are almost as one point in Figure 20.

This isentropic rule is valid also for other PE structural characteristics: molecular mass and its distribution, chain branching (ethyl, butyl, amyl and longer), unsaturated bonds: The same PE structure and properties are obtained if the entropy of ET under polymerization conditions is the same, regardless the differences in other polymerization conditions, i.e. reactor type, pressure, temperature and method of initiation. Hence, the common lines were obtained for the main structural characteristics (Table 4).

It is possible to predict PE structure and density for any polymerization pressure and temperature reading S/S_c from [26] and using expressions from Table 4. And vice versa, in order to produce PE with desired structure and density, it is necessary to calculate S/Sc from expressions in Table 4 and to read from thermodynamic diagram [26] what should be reactor operating pressure and temperature to achieve the calculated value of entropy.

It should be emphasized that from high ordered ("crystalline") γ-ET the high ordered PE originates, i.e. high crystallinity, density and molecular mass and wide MWD, almost linear PE, low degree of branching and unsaturation. From disordered β-ET the disordered PE originates, i.e. low crystallinity, density and molecular mass and narrow MWD, but high degree of branching and unsaturation. In other words, there is "mother – daughter" resemblance between monomer and polymer. There is a genetic correlation between monomer organization and polymer structure and properties. For example, the "crystalline" γ phase of ethylene ("mother") is transformed by heating from order to disordered β phase at those P-T conditions which correspond to S/Sc = 1. Also, the crystallite of its "daughter" polyethylene is melted at the same P-T conditions (Figure 21).

EXPANSION TO OTHER FLUIDS AND POLYMERIZATION SYSTEMS

It is important to notice that for the proposal of supramolecular particles and derivation of our model of the physical and chemical state of ethylene we used [4]:
(a) Only two empirical parameters (r_e and b) and data of ethylene molecule dimensions;
(b) Simple mathematical expressions for the volumes

Figure 20. Effect ET entropy under polymerization conditions on PE density [4,29].

Table 4. Effects of ethylene entropy (S/S_c) [26] under polymerization conditions on branching, unsaturated bonds and density of PE [41].

Structural characteristic	Mathematical expression	Standard error	Correlation coefficient
Short chain branches	$CH_3/1000\ C = \exp^{(6.825\ S/Sc - 4.887)}$	2.67	0.954
Ethyl branches	$Et/1000\ C = 3.176 + 0.0074\ (S/Sc)^{32.56}$	0.94	0.981
Butyl branches	$Bu/1000\ C = 37.549\ (S/Sc) - 34$	1.00	0.959
Amyl and longer	$(Am+Longs)/1000\ C = 32.926\ (S/Sc) - 30.7$	1.04	0.941
Vinylidene groups	$CH_2=C</1000\ C = 0.042 + 0.01\ (S/Sc)^{20.76}$	0.02	0.984
Transvinylidene groups	$-CH=CH-/1000\ C = 0.009 + 0.0013\ (S/Sc)^{20.73}$	0.03	0.954
Density	$d\ (kg/m^3) = 1030.7 - 100.18\ (S/Sc)$	3.12	0.953

of sphere and cylinder;

(c) Rule that some movable particles can exist as long as there is enough space for their movement; as the compression reduces free volume of gas, the particles which require more space are one by one transformed to new particles that require less space for movement, whereby a part of the external movement of the molecule turns into the movement of its inner parts.

For supramolecular ethylene particles we observed the following [4,23,53]:

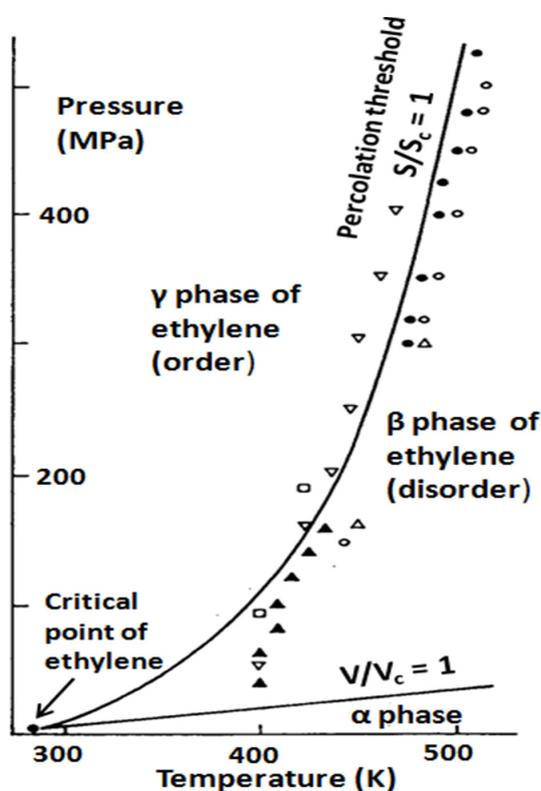Observation 1. The volumes of supramolecular

Figure 21. Phase changes in pure ethylene (percolation threshold line $S/Sc = 1$) and in pure polyethylene (points) occur at the same pressure-temperature conditions. (References for polyethylene melting at high pressure are in [4,29,30].)

particles of ethylene are close to its volumes in definite characteristic states:

(a) The volume of the rotating molecular pair (V_p = 127.6 cm³/mol) calculated on the basis of the experimental value for equilibrium distance r_e according to the Lennard-Jones model is equal to the critical volume (V_c = 127.6 cm³/mol), i.e. $V_p = V_c$.

(b) The molar volume of the bimolecule is equal to the co-volume, i.e. van der Waals constant b = 57.1 cm³/mol.

(c) The molar volume of the rotating oligomolecules (V_{om} = 37.8 cm³/mol), calculated by dimensions of the ethylene molecules, is approximately equal to the molar volume of ethylene solid phase at the triple point V_{ts} = 39.08 cm³/mol.

Observation 2. The relations between the ethylene molar volumes in the characteristic states, as well as the relations between the volumes of the supramolecular particles of ethylene, are in the form of the exponent 2^n which is in agreement with theory of Savich and Kashanin about the behaviour of matter at high pressures [38].
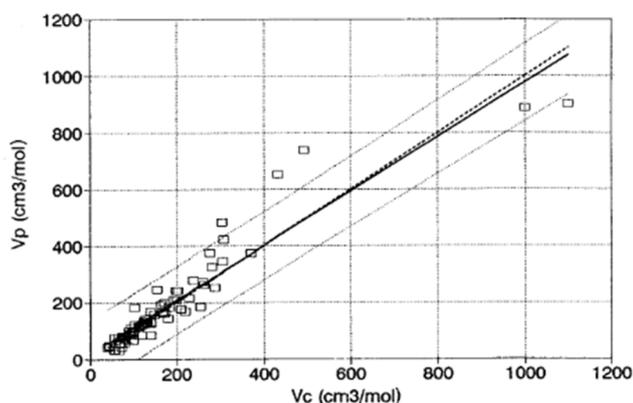
(a) The volume of the rotating individual molecules V_M = 222 cm³/mol is approximately twice the critical volume, i.e. $V_M \cong 2\ V_c$.

(b) The volume of the bimolecule is approximately twice that of the critical volume V_c, i.e. $b \cong V_c/2$.

(c) The volume of ethylene at 0 K (V_0 = 35.7 cm³/mol) is approximately four times less than the critical volume, i.e. $V_0 \cong V_c/4$.

We found [53] that observations 1 and 2 are valid for other 144 substances, including chemical elements, inorganic and organic compounds. We derived a mathematical model that described the correlation between characteristic volumes of matter and

concluded that the fluids of other substances have the same supramolecular structure like ethylene (Figure 12), but the phase transitions are at different values of pressure, temperature and volume. For example, observation 1(a) that the volume occupied by rotation of a molecular pair V_p is equal to the critical volume of ethylene is not accidental. Based on the experimental data [9] for r_e of 92 substances we calculated V_p by Eq. 3 and proved that V_p was equal to their empirical values of V_c [53] (Figure 22). The points are situated around the bisector line. On this base, it can be concluded that for all substances the critical volume is equal to the volume of the sphere occupied by rotation of a molecular pair, whereby the radius of the sphere is equal to the equilibrium parameter re for Lennard-Jones's model. Like for ethylene at α-β phase transition (Figures 9 and 10), other substances have a ridge of heat capacity close to critical isochore, so called Widom line [54,55].

The additional supercritical liquid to gas boundaries are proposed for other substances, e.g. Frenkel line [55], which separates two phases of liquids, i.e. "non-rigid" at higher and "rigid" at lower temperatures. According to our results [21-23,36,39,47], for ethylene and other substances, β phase can be considered as "non-rigid" and γ phase is "rigid" liquid. γ phase is composed of two micro phases: continuous oligomolecular ("crystal like") in which bimolecular domains ("gas like") are dispersed.

Recently, Korolev et al. [56] has experimentally

confirmed for 8000 organic compounds that by the condensation of vapor below critical point (i.e. from ideal gas to liquid crossing line c in Figure 1) the monomer molecules from vapor pass into liquid as dimers. By further cooling linear oligomers are formed, and at even lower temperatures the molecules are all mutually connected forming a continuous associative structure. We reached the same conclusion by analyzing the path above critical point (Figure 1, line d) and Figure 12: ideal gas → α phase → β phase → γ phase → liquid. Whatever is the path, the liquid structure has to be the same for the same P, V, T conditions.

Knowing supramolecular organization of liquid monomers, we explained the mechanism and kinetics of free radical polymerization of alkylmethacrylates [23,36,39,47,57-59] and styrene [60,61].

It is well known that there is self-assembling of molecules during the adsorption on supports [62]. By increasing the support surface coverage, the surface pressure is increased and adsorbate layer is transformed from two-dimensional mobile lattice gas to liquid and finally to high organized sold phase. Hence, we applied this comprehension to develop the charge percolation mechanism [36,39,48,63,64] of olefins polymerization by transition metal complexes, e.g. Ziegler-Natta, Phillips and metallocene catalysts.

ACKNOWLEDGMENT

Figure 22. Volumes of molecular pairs V_p calculated by Eq. 3 are equal to the empirical values of critical volumes V_c [53]. □ empirical data; — Regression; ---- Expected; ⋯⋯ Confidence limits. Standard error is 60.1 cm³/mol; Correlation coefficient 0.94. (Based on the empirical data [9] for 92 substances for r_e and V_c).

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