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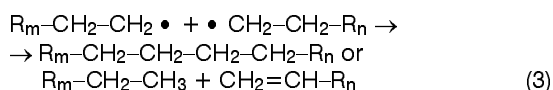
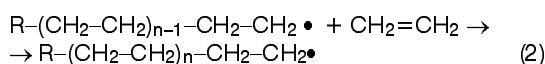
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COMPRESSED ETHYLENE PHASE STATES AND THEIR IMPORTANCE FOR THE PRODUCTION OF LOW DENSITY POLYETHYLENE*

In the last three decades the authors have published papers on the concept of the supra-molecular organization and the phase state of compressed ethylene gas and their effects on the mechanism and kinetics of free-radical ethylene polymerization. The effects on the macromolecular structure of low density polyethylene (LDPE) were also explained. The importance of the phase state of compressed ethylene on the industrial process of LDPE production are presented in this paper: The start-up of polymerization, the peak in the polymerization rate curve, the stability of the reaction, the structure and properties of LDPE, the separation of unreacted ethylene and polyethylene and ethylene compression are discussed.

It is well known that ethylene can be polymerized by a free radical mechanism. There are three basic reactions, i.e. chain initiation, chain growth and its termination. The initiation is performed by the addition of some initiators, usually organic peroxides RO-OR or oxygen, which decompose and produce the initial free radicals RO• (1). It has generally been accepted that chain propagation includes the addition of ethylene molecules one by one to the growing radicals (2). The termination reaction (3) includes the coupling or disproportion of growing radicals, both of them resulting in dead polyethylene chains.



The peculiarity of this process, discovered in 1933, is that it can only be performed at very high pressures of ethylene gas, usually 1000–2000 bars. In spite the great development of this process for the commercial production of low density polyethylene (LDPE), the main open question was how to explain the role of high pressure in this process. We have explained [1–7] that the role of pressure is to enable the formation of various supra-molecular species of ethylene (Figure 1). The basic rule is that by the increase of pressure, i.e. by the decrease of free volume, rotating species are formed since they need less space for movement. There are several

phases in compressed ethylene: the ideal gas at low pressures consists of individual translating and rotating molecules; the α phase (a mixture of individual rotating molecules and rotating molecular pairs); the β phase (rotating molecular pairs and rotating bimolecules) and the γ phase (rotating bimolecules and oligomolecules). The transition from the α to the β phase occurs at the

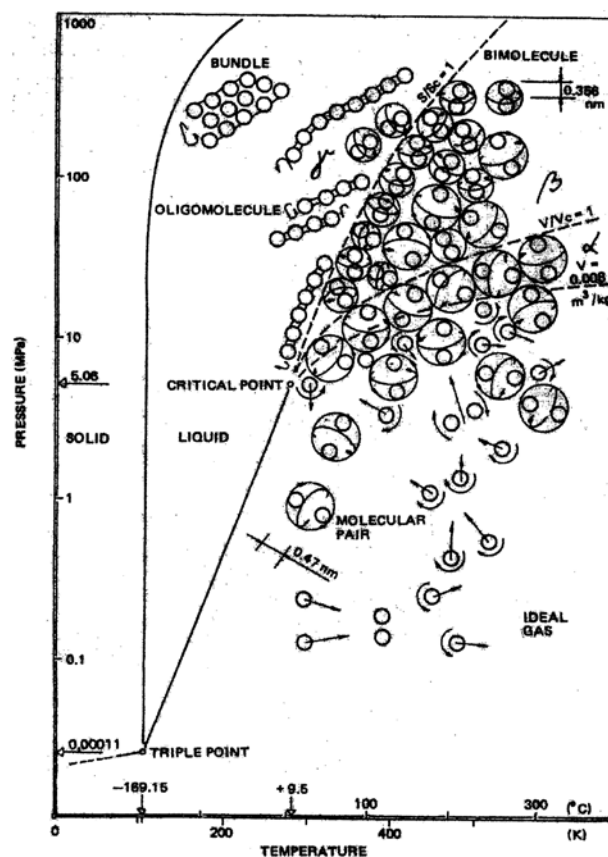


Figure 1. Phase state and rotating supra-molecular species of compressed ethylene gas [1–5]

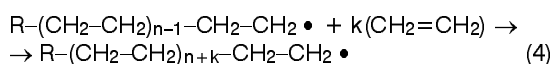
Slika 1. Fazno stanje i rotirajuće nadmolekulske čestice gasovitog etilena [1–5]

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critical isochore ($V/V_c=1$), and from the β to the γ phase at the critical isentrope ($S/S_c=1$) conditions. The thermodynamic, physical and spectroscopic evidence on ethylene self-organization and phase changes by compression has been presented elsewhere [1,2].

The supra-molecular species exhibit decisive effects on the polymerization mechanism, the kinetics and on the LDPE structure. The individual molecules and the molecular pairs are unable to polymerize. Hence, polymerization is not possible in the α phase. The bimolecules polymerize easily, while the oligomolecules polymerize after some initial induction period [3]. In these cases, the polymerization could be explained by the theory of organized monomer polymerization developed by Kargin and Kabanov [10]. Hence, the propagation presented by reaction (2) should be modified and presented by reaction (4) where $k = 2$ and $k > 2$ for bimolecules and oligomolecules, respectively.



ETHYLENE PHASE STATES IN DIFFERENT STEPS OF LDPE PRODUCTION PROCESSES

Regardless of some discrepancies, all LDPE production processes include the three main steps [8] (Figure 2): a) Ethylene compression up to 1000–3000 bars; b) Ethylene polymerization in a continuous flow stirred autoclave or in tubular reactors at 1000–3000 bars and 150–300°C and c) Separation of polymer from unreacted ethylene in high pressure (150–300 bars) and in low pressure (1–2 bars) separators. Afterwards, ethylene is recycled to the compressors, and LDPE is extruded and cut into pellets. If the operating conditions of these steps are plotted in the diagram of the phase state of ethylene, it is obvious that ethylene passes through all phase states during compression (Figure 3). Polymerization is carried out in the β -phase and in the γ -phase. The separation of unreacted ethylene from LDPE is in the α -phase.

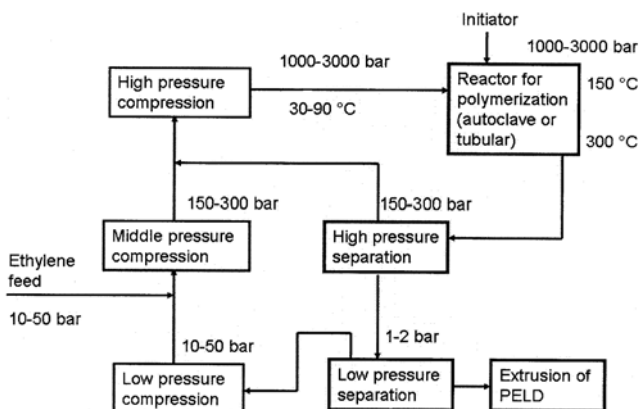


Figure 2. Scheme of the LDPE production process

Slika 2. Šema procesa proizvodnje LDPE

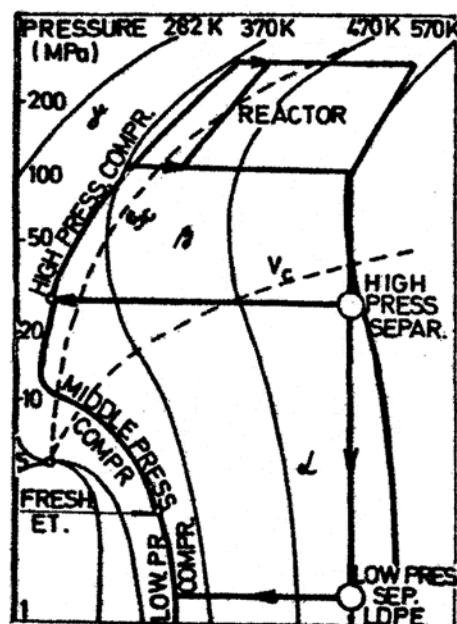


Figure 3. Ethylene phase state in different steps of the LDPE production process

Slika 3. Fazno stanje etilena u različitim stupnjevima procesa proizvodnje LDPE

The effects of ethylene phase states on the compression steps, the reaction start-up, the reaction stability and the separation of polymer from unreacted ethylene as well as on the LDPE structure prediction are presented in this paper.

START-UP OF POLYMERIZATION

The polymerization is started by the injection of an initiator (organic peroxide or oxygen). For a successful start-up it is necessary to have the highest concentration of the very polymerizable bimolecules, i.e. the reaction conditions should be close to the β - γ phase transition, but in the β phase, since initiation in the γ phase is followed by an induction period [3]. Industrial experience has shown that the most convenient conditions for start-up are 1200 bar and 140°C for an autoclave and 2500 bar and 180°C for tubular reactors [9]. These operating conditions are indeed close to the β - γ phase transition, as proposed.

PEAK IN THE POLYMERIZATION RATE CURVE

According to the theory of polymerization of organized monomers, the highest polymerization rate (R_{pol}) should be expected close to the phase transition conditions [10,11]. In the case of ethylene polymerization, it has been proved that a maximum of the R_{pol} was obtained at the conditions of the β - γ phase transition [3,4] (Figure 4). The initiator consumption should have a minimum value at the same condition. The experimental data [12] confirm these predictions that are very important from the commercial point of view.

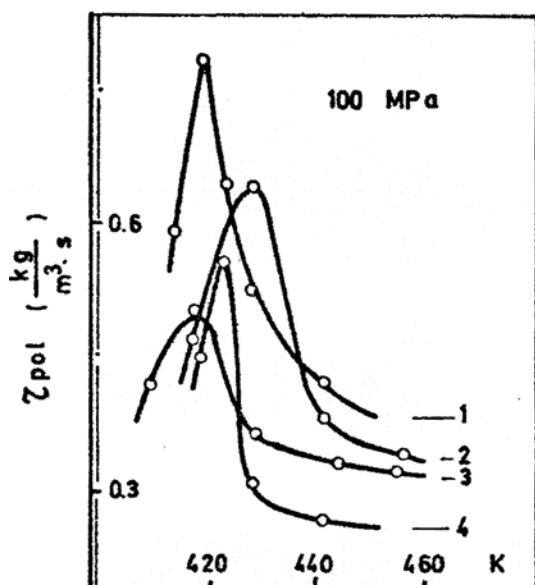


Figure 4. Effect of temperature on the polymerization rate initiated by four different peroxides [18]. (the β - γ phase transition temperature is 410 K at 100 MPa).

Slika 4. Uticaj temperature na brzinu polimerizacije inicirane sa četiri različita peroksida [18]. (Pri pritisku 100 MPa je fazni prelaz β - γ na temperaturi 410 K).

STABILITY OF THE REACTION

Although the conditions near the β - γ phase transition are convenient for the reaction start-up and for initiator consumption, they are very inconvenient in respect to reaction stability [13]. If the conditions correspond to the γ phase, an accidental change of temperature in the reactor will cause either the end of the reaction or an uncontrolled auto-acceleration of the reaction. If the operating conditions correspond to the β phase, an accidental change of temperature will cause its oscillations that can be damping or progressive. The experimentally observed reaction instabilities [14,15] are the evidence for such predictions.

LDPE STRUCTURE AND PROPERTIES

The degree of ethylene order, inversely proportional to the entropy, has a decisive effect on the macro-

molecular structure and properties of LDPE [5-7,16]. Despite the differences in polymerization conditions (pressure, temperature and method of initiation), an equal macromolecular structure is obtained if the entropy of ethylene is equal. This *isentropic rule* is valid for the different types of short branches (ethyl, butyl, amyl), unsaturated bonds, long chain branches, molecular mass, molecular mass distribution and the density of LDPE. Based on the isentropic rule and published experimental data, mathematical models have been derived that relate the structure and density of LDPE with the ethylene entropy [17] under the polymerization conditions (Table 1). These mathematical models enable the prediction of LDPE structure and properties produced under any polymerization conditions. They also make it possible to select the polymerization conditions for the production of LDPE with the desired structure and properties.

UNREACTED ETHYLENE AND POLYETHYLENE SEPARATION

During the separation of unreacted monomer from polyethylene it is important to prevent further ethylene polymerization resulting in the formation of low molecular mass waxes that can deteriorate the quality of LDPE. That means that such operating conditions should be chosen in which non-reactive molecular pairs and individual molecules of ethylene exist. These conditions correspond to the α phase of ethylene. Indeed, such conditions are achieved in typical industrial processes (Figure 3).

ETHYLENE GAS COMPRESSION

It is important to prevent ethylene polymerization in the compressors and in the pipes. That means that the β - γ phase transition should be avoided in that part of the installation. Otherwise, the presence of even a low quantity of initiators, as well as very reactive bimolecules of ethylene, could initiate undesirable polymerization in the compressors and high pressure tubes. The plugging of pipes by polyethylene described in [8] could be attributed to operation close to the β - γ phase transition.

Table 1. Effects of ethylene entropy (S/Sc) [17] on the structure and density of LDPE (S/Sc) [17] under the polymerization conditions
Tabela 1. Uticaji entropije etilena (S/Sc) [17] u uslovima polimerizacije na strukturu i gustinu LDPE (S/Sc) [17]

Structural characteristic	Mathematical expression	Standard error	Correlation coefficient
Short chain branches	$CH_3 / 1000 C = \exp^{(6.825S/Sc - 4.887)}$	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

CONCLUSIONS

The ethylene phase state has decisive effects on all steps of LDPE production processes. By knowing these effects, better understanding of the production process is possible. More successful trouble shooting, enhanced control of LDPE structure and properties, as well as further process improvements are enabled.

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IZVOD

FAZNO STANJE KOMPROMOVANOG ETILENA I NJEGOV ZNAČAJ ZA PROIZVODNJU POLIETILENA NISKE GUSTINE

(Naučni rad)

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U prethodne tri dekade, autori su objavili koncept nadmolekulske organizacije i faznog stanja komprimovanog gasovitog etilena i njihov uticaj na mehanizam i kinetiku polimerizacije pomoću slobodnih radikala. Takođe su objašnjeni uticaji na strukturu makromolekula polietilena niske gustine (PELD). U ovom radu je prikazan značaj faznog stanja komprimovanog etilena za industrijski proces proizvodnje PELD: započinjanje polimerizacije, najveću brzinu polimerizacije, stabilnost reakcije, strukturu i svojstva PELD, razdvajanje neproreagovalog etilena od polietilena i komprimovanje etilena.

Ključne reči: Komprimovani etilen • Fazno stanje • Polimerizacija • polietilen niske gustine • Tehnologija proizvodnje •

Key words: Compressed ethylene • Phase state • Polymerization • Low density polyethylene • Production technology •