

Bifunctional Nickel- or Cobalt-containing Catalyst-stabilizers for Polybutadiene Production and Stabilization (Part I): Kinetic Study and Molecular Mass Stereoregularity Correlation

Fizuli Akbar Nasirov*

Institute of Petrochemical Processes, Azerbaijan National Academy of Sciences,
Baku-370025, Republic of Azerbaijan

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ABSTRACT

The polymerization of butadiene with catalytic dithiosystems, based on organic dithio derivatives of Ni or Co and organoaluminium compounds was studied. It was shown that these catalytic dithiosystems provide the preparation of the low- and high-molecular weight 1,4-cis-polybutadienes; high-molecular weight 1,4-cis + 1,2- and syndiotactic 1,2-polybutadienes with high activity. The effect of nickel or cobalt and monomer concentration, Al:Co ratio, temperature, polymerization time on conversion, stereoregularity and molecular weight in the butadiene polymerization by nickel- and cobalt-containing dithiosystems was studied. The regularities of interrelated changes of polybutadiene microstructure and molecular masses in synthesis in the presence of nickel- and cobalt-containing dithiosystems have been investigated and explained.

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Key Words:

Nickel- or cobalt-dithioderivatives;
organoaluminium; dithiosystems;
butadiene polymerization;
polybutadiene; kinetic regularities;
molecular mass-stereoregularity
correlation.

INTRODUCTION

The polymerization of butadiene to high stereoregular polymers is achieved only by using Ziegler-Natta type co-ordination catalysts.

Industrially titanium, nickel or cobalt compounds, together with organoaluminium compounds, are

generally used.

These systems have been studied by a number of authors, including Dolgoplosk and Tinyakova [1], Bawn [2], Ashitaka [3], Gippin [4], Saltman and Kuzma [5], Diaconescu and Medvedev [6], Honig [7-9], and

(*) To whom correspondance should be addressed.
E-mail: fizulin52@hotmail.com

Hsu et al. [10-16].

But these catalytic systems suffer such disadvantages as low activity, poor conversions, relatively severe operating conditions, poor selectivity, short catalyst lifetime, etc.

The existing industrial stereoregular polybutadiene production processes are characterized also by the great amounts of wastes (conditioned by a stage of washing catalyst oddments from polymer) and formation of smelling oligomers.

For modern applications high activity and selectivity catalysts, which operate at about ambient temperature and atmospheric pressure to produce various types of polybutadienes are desirable.

The objective of this paper is to provide information regarding the catalytic activity and stabilization effectiveness of a new generation of bifunctional metal complex catalyst-stabilizers for butadiene polymerization with simultaneous stabilization of the end product.

In Part I of this article we discuss the catalytic activity of nickel- or cobalt-containing catalytic systems depending on ligand surrounding the transition metals and the influence of various catalyst components and monomer levels on conversion and molecular mass-stereoregularity correlation in the polymerization of butadiene.

EXPERIMENTAL

Materials

Polymerization was conducted with toluene as a solvent. After predrying over metallic sodium for 24 h, toluene was distilled over metallic sodium and preserved under Na (stored in the calibrated reservoir under metallic Na as well).

The butadiene, supplied by Yefremov Synthetic Rubber Plant (Russian Federation), was analyzed by gas chromatography and found to have the purity 99.5% (wt). Although the moisture content was found to be less than 15 ppm by Karl Fischer, it was established that water levels need to be controlled within 1 ppm using further drying effected by molecular sieves. Traces of inhibitor were removed with soda asbestos.

Alkylaluminium halides (AAH)-diethylaluminium-chloride (Et_2AlCl -DEAC), ethylaluminium sesquichloride ($\text{Et}_3\text{Al}_2\text{Cl}_3$ -EASC) obtained from Redkino plant (Moscow, Russian Federation) with a mini-

mum purity of 85 % (wt), were used as they were received. The DEAC (or EASC), diluted to 10 % (vol.) in dry toluene for polymerizations, was drawn from a crown-sealed beverage bottle kept in a glove box.

Organic dithioderivatives (dithiophosphates, dithiocarbamates and xanthogenates) of nickel and cobalt have been synthesized according to refs. 17-19. The characteristics of the synthesized dithioderivatives are shown in Table 1.

Polymerization Procedure

Where necessary, manipulations were carried out under dry, oxygen-free argon or nitrogen in Schlenk-type apparatus with appropriate techniques and gas tight syringes.

The desired volume of toluene, monomer, DEAC (or EASC) and nickel or cobalt components solutions were added to the reactor continuously from the calibrated glass reservoir with stirring and temperature control were initiated. In a typical experiment, the reaction vessel, such as glass ampoule or dilatometer, was evacuated whilst hot, allowed to cool and then filled with dry, oxygen-free argon or nitrogen.

The usual order of addition was: solvent, monomer, nickel or cobalt component and finally aluminium organic compound at -78 C . All polymerizations were conducted at $15\text{-}60\text{ C}$.

After polymerization the polymerizate was poured to ethanol and the reaction was terminated. The precipitated polymer was (if it is necessary) washed several times with ethanol. The polybutadiene was dried at 40 C in a vacuum to constant weight and stored under argon or nitrogen.

Molecular Weight and Structure Determinations

The molecular mass was determined by viscosimetry method [3, 20] with relationships:

$$[\eta]_{(\text{toluene})}^{25} = 3.9 \times 10^{-5} \cdot M^{0.99} \text{ for low MM 1,4-cis-PBD;}$$

$$[\eta]_{(\text{toluene})}^{30} = 3.05 \times 10^{-4} \cdot M^{0.725} \text{ for high MM 1,4-cis-PBD;}$$

$$[\eta]_{(\text{toluene})}^{30} = 15.6 \times 10^{-5} \cdot M^{0.75} \text{ for high MM 1,4-cis + 1,2-PBD;}$$

$$[\eta]_{(\text{tetralin})}^{135} = 9.41 \times 10^{-5} \cdot M^{0.854} \text{ for high MM and highly crystalline PBD.}$$

The molecular mass was also found by a gel permeation chromatograph (GPC), constructed in Czech Republic with a 6000A pump, original injector, R-400 differential refractive index detector, styragel columns

Table 1. Physico-chemical and analytical data of dithiocompounds used.

| Nomenclature | Chemical formula | Complex | Yield (% by mass) | Melting point (°C) | Molecular mass, found/calcd. | Elemental composition, found / calcd. | | | |
|--------------|------------------|--|----------------------|----------------------------|---------------------------------|--|-------------|---------------|---------------|
| | | | | | | C | H | P | S |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| DEDTPh-Ni | a | Nickel <i>O,O'</i> -diethyl dithiophosphate | 75 | 105 | 428.5 / 429.05 | 22.42 / 22.40 | 4.68 / 4.7 | 14.47 / 14.92 | 28.96 / 29.89 |
| DPhDTPh-Ni | b | Nickel <i>O,O'</i> -diphenyl dithiophosphate | 90 | 126 | 622.0 / 620.7 | 46.23 / 46.40 | 3.18 / 3.22 | 9.72 / 9.99 | 20.73 / 20.62 |
| TBDTPh-Ni | c | Nickel <i>O,O'</i> -diethyl-4-tert. butylphenyl dithiophosphate | 87 | 222 | 842.0 / 844.7 | 56.47 / 56.82 | 6.29 / 6.16 | 7.32 / 7.34 | 15.36 / 15.15 |
| DEDTC-Ni | d | Nickel <i>N,N'</i> -diethyl dithiocarbamate | 96 | T _{dec.} > 250 | 356.0 / 355.23 | 33.7 / 33.81 | 5.61 / 5.68 | — | 35.96 / 36.1 |
| DiPDTPh-Co | e | Cobalt <i>O,O'</i> -diiso-propyl dithiophosphate | 92 | — | 485.0 / 485.0 | 29.69 / 29.75 | 5.77 / 5.85 | 12.78 / 12.91 | 26.39 / 26.56 |
| CTPh-Co | f | Cobalt <i>O,O'</i> -di-4-methyl-phenyl dithiophosphate | 75 | 107 | 676.0 / 677.0 | 49.33 / 49.64 | 4.21 / 4.14 | 8.85 / 9.16 | 18.75 / 18.91 |

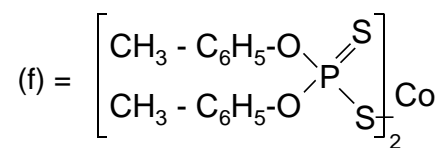
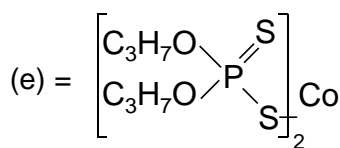
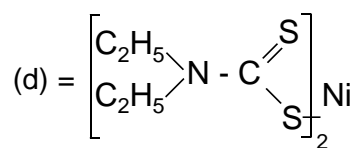
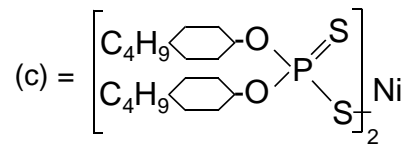
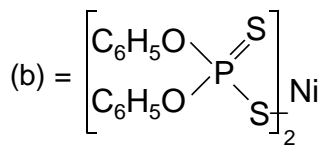
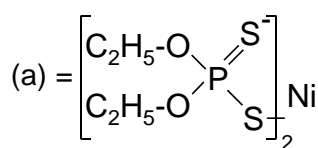


Table 1 continued

Table 1 continued

| Nomenclature | Chemical formula | Complex | Yield (% by mass) | Melting point (°C) | Molecular mass, found/calcd. | Elemental composition, found / calcd. | | | |
|---------------|------------------|--|----------------------|-----------------------|---------------------------------|--|-------------|---------------|---------------|
| | | | | | | C | H | P | S |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| TBDTPH-Co | g | Cobalt <i>O,O'</i> -di-4- <i>t</i> -butylphenyl dithiophosphate | 82 | 192 | 841.0/ 844.9 | 56.6/ 56.8 | 5.9/ 6.1 | 7.18/ 7.34 | 15.4 15.2 |
| DPhDTPH-Co | h | Cobalt <i>O,O'</i> -diphenyl dithiophosphate | 85 | 136 | 618.0/ 620.9 | 46.1/ 46.3 | 3.3/ 3.2 | 9.87/ 9.98 | 20.5/ 20.6 |
| TBPh-Co | i | Cobalt 2,2'-thio-bis- <i>O,O'</i> -di-4- <i>t</i> -butylphenyl dithiophosphate | 80 | 276 | 905.1/ 905.0 | 53.2/ 53.0 | 5.2/ 5.3 | 6.71/ 6.85 | 21.5/ 21.2 |
| TBOPH-Co | j | Cobalt 2,2'-thio-bis- <i>O,O'</i> -di-4- <i>t</i> -octylphenyl dithiophosphate | 70 | 235 | 1129/ 1128 | 59.8/ 59.5 | 6.9/ 7.1 | 5.33/ 5.48 | 17.1 17.0 |
| 4,6-TBF-Co | k | Cobalt 2,2'-thio-bis- <i>O,O'</i> -di-4,6- <i>t</i> -butylphenyl dithiophosphate | 75 | 186 | 1129/ 1129 | 59.8 59.5 | 7.1/ 7.0 | 5.85/ 5.48 | 16.9 17.0 |
| 4m, 6-TBPh-Co | l | Cobalt <i>O,O'</i> -di-4-methylphenyl dithiophosphate | 61 | 200 | 960.0/ 961.0 | 54.8/ 54.9 | 6.1/ 5.8 | 6.21 6.46 | 19.4 19.8 |

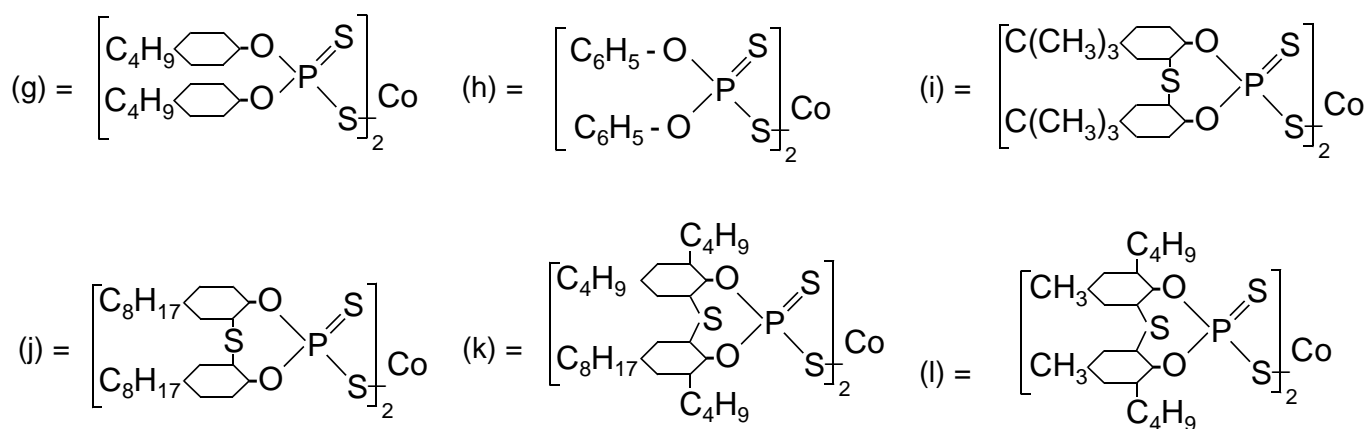
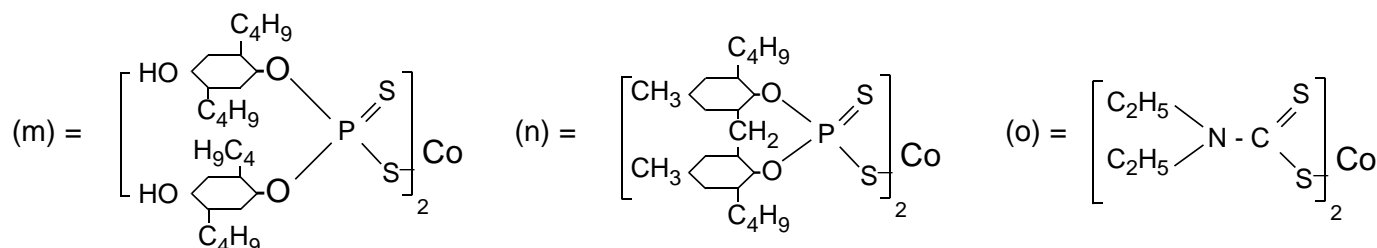


Table 1 continued

Table 1 continued

| Nomenclature | Chemical formula | Complex | Yield (% by mass) | Melting point (°C) | Molecular mass, found/calcd. | Elemental composition, found / calcd. | | | |
|--------------|------------------|--|----------------------|-----------------------|---------------------------------|--|-------------|---------------|---------------|
| | | | | | | C | H | P | S |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| X-Co | m | Cobalt <i>O,O'</i> -di-(3,5-di- <i>t</i> -butylphenyl-4-hydroxyphenyl) dithiophosphate | — | — | 1135/ 1132 | 59.8/ 59.3 | 7.5/ 7.4 | 5.60/ 5.47 | 11.4 11.3 |
| NGDTPH-Co | n | Cobalt <i>O,O'</i> -di-(2,2'-methylene-bis-4-methylene-6- <i>t</i> -butylphenyl) dithiophosphate | 87 | — | 856.2/ 857.0 | 55.9/ 56.4 | 6.8/ 7.0 | 7.16/ 7.2 | 14.8/ 14.9 |
| DEDTC-Co | o | Cobalt <i>N,N</i> -dimethyl dithiocarbamate | — | $T_{dec.} > 245$ | 355.0/ 356.0 | 33.8/ 33.9 | 5.6/ 5.8 | — 1 | 36.1/ 36.2 |



with nominal exclusion of $500, 10^3, 10^4, 10^5, 10^6$. The GPC was operated at a flow rate of $0.8 \text{ mL} \cdot \text{min}^{-1}$ with toluene as solvent. The sample concentration was kept at about 0.3-0.6 % with a sample volume of 100-200 μL .

GPC Instrument was calibrated according to the universal calibration method by using narrow molecular weight polystyrene standards [21].

Structures of polybutadienes were determined by IR-spectrometry method [22,23].

RESULTS AND DISCUSSION

The catalytic activity of several samples of the nickel and cobalt organic dithioderivatives together with organoaluminium compounds (nickel or cobalt

dithiosystems) was investigated and the results are summarized in Table 2 in comparison with the known compounds, such as stearate, palmitate, acetyl acetate, naphthenate of nickel and cobalt. The data demonstrate that these nickel and cobalt dithiosystems are by 3-20 times more active than the known systems in the catalytic polymerization of butadiene.

Nickel-containing dithiosystems (Ni-DTPH, Ni-DTC or Ni-Xh + AAH) provide the preparation of low molecular (liquid) 1,4-cis-PBD with 1,4-cis content 78-84 % and MM 1600-4100. Their production capacity is 27.0 kg of PBD per 1 g Ni in an hour, but the known systems have 3.5 kg of PBD/g Ni per h [24- 26].

Cobalt dithiophosphate catalytic systems (cobalt dithiophosphates + AAH) would produce the high molecular 1,4-cis-PBD with MM 150,000-400,000 and

1,4-cis content 87-98 %. Productivity of these systems is 109.0 kg of PBD/g Co per h, against 0.1-12.0 kg PBD/g Co per h in the known systems [27, 28].

Cobalt dithiocarbamate catalytic systems (cobalt dithiocarbamates + AAH) produce the high molecular

(100,000-350,000) 1,4-cis + 1,2-PBD with 1,4-content 60-65 %, 1,2-content 30-40 % and productivity-10.0 kg of PBD/g Co per h [24].

Cobalt xanthogenate catalytic systems (cobalt xanthogenates + TAA) give high molecular and highly

Table 2. Comparison of efficiency of different nickel- and cobalt-containing catalytic systems MeX_2 + DEAC in the butadiene polymerization process. Conditions: $[\text{M}] = 3 \text{ mol/L}$, $\text{Al: Me} = 100: 1$, $T = 25^\circ\text{C}$, solvent - toluene.

| ItemNo | Nickel or cobalt compounds (MeX_2) | Concentration of (MeX_2), $\text{Me} \cdot 10^4$ (mole/L) | Reaction time (min) | Yield (% by mass) | Intrinsic viscosity, $[\eta]$ (dL/g) | Molecular mass, $\text{M} \cdot 10^{-3}$ | | Microstructure (%) | | | Yield of polymer per 1 g of transition metal per hour (kg) |
|--------|--|--|---------------------|-------------------|--------------------------------------|--|-------------|--------------------|-----------|------|--|
| | | | | | | \bar{M}_v | \bar{M}_n | 1,4-cis | 1,4-trans | 1,2- | |
| 1 | DEDPh-Ni | 10 | 5 | 78 | 0,08 | 2.5 | 1.4 | 82 | 16 | 2 | 27 |
| 2 | DPhDTPH-Ni | 10 | 10 | 80 | 0.1 | 3.1 | 1.7 | 80 | 17 | 3 | 14 |
| 3 | TBDTPH-Ni | 10 | 20 | 60 | 0.13 | 4.1 | 2.3 | 84 | 14 | 2 | 5 |
| 4 | DEDTC-Ni | 10 | 15 | 80 | 0.06 | 1.6 | 0.9 | 78 | 20 | 2 | 10 |
| 5 | DiPDTPH-Ni | 10 | 10 | 74 | 1.32 | 100 | 55 | 88 | 9 | 3 | 12 |
| 6 | CTPh-Co | 10 | 30 | 98 | 1.62 | 138 | 76 | 80 | 18 | 2 | 7 |
| 7 | TBDTPH-Co | 10 | 10 | 66 | 1.6 | 140 | 109 | 90 | 7 | 3 | 109 |
| 8 | DPhDTPH-Co | 1 | 30 | 44 | 2.5 | - | 250 | 93 | 5 | 2 | 24 |
| 9 | TBPh-Co | 1 | 30 | 73 | 1.0 | - | 50 | 87 | 7 | 6 | 40 |
| 10 | TBOPH-Co | 1 | 30 | 82 | 1.7 | - | 125 | 88 | 8 | 4 | 45 |
| 11 | K-TBPh-Co | 1 | 30 | 17 | 1.1 | - | 61 | 89 | 3 | 8 | 9 |
| 12 | 4m-6-TBPh-Co | 1 | 15 | 54 | 1.5 | - | 100 | 92 | 5 | 3 | 59 |
| 13 | 4,6-TBPh-Co | 1 | 20 | 51 | 2.4 | - | 236 | 93 | 5 | 2 | 42 |
| 14 | X-Co | 1 | 15 | 52 | 2.1 | - | 181 | 91 | 5 | 4 | 57 |
| 15 | NGDTPH-Co | 1 | 30 | 83 | 3.7 | - | 393 | 98 | 1 | 1 | 46 |
| 16 | DEDTC-Co | 10 | 20 | 48 | 1.95 | 174 | 96 | 58 | 8 | 34 | 44 |
| 17 | EtXh-Co | 2 | 60 | 50 | 2.3 | - | 220 | 96 | 2 | 2 | - |
| 18 | BuXh-Co | 2 | 60 | 80 | 2.5 | - | 255 | 95 | 2 | 3 | - |
| 19 | EtXh-Co | 2 | 60 | 95 | 2.2 | - | - | 2 | 1 | 97 | - |
| 20 | i-PrXh-Co | 2 | 60 | 98 | 2.3 | - | - | 1 | 1 | 98 | - |
| 21 | BuXh-Co | 2 | 60 | 99 | 2.5 | - | - | 1 | - | 99 | - |
| 22 | Ni (stearate) ₂ | 1 | 30 | 60 | 0.12 | 3.6 | 2 | 78 | 20 | 2 | 3.5 |
| 23 | Ni (palmitate) ₂ | 1 | 60 | 70 | 0.37 | 12.0 | 6.5 | 81 | 17 | 2 | 3 |
| 24 | Ni (acac) ₂ | 10 | 60 | 60 | 0.2 | 6.2 | 3.5 | 80 | 17 | 3 | 2 |
| 25 | Ni (naphthenate) ₂ | 10 | 20h | 78 | 0.09 | 2.8 | 1.6 | 72 | 26 | 2 | 0.7 |
| 26 | Co (naphthenate) ₂ | 10 | 60 | 65 | 2.0 | - | 200 | 90 | 6 | 4 | 12 |
| 27 | CoCl ₂ .Py (3:2) | 10 | 16h | 94 | 2.67 | - | 250 | 95 | 3 | 2 | 0.1 |
| 28 | Co (acac) 3+TEA+ + H ₂ O + CS ₂ [3] | 4.5 | 30 | 20 | 2.7* | - | - | 1 | - | 99 | 1.2 |

Note: Experiments 19-21: a) organoaluminium compound is TEA; b) intrinsic viscosity in tetralin at 135°C (* also exp. 28); $\bar{M}_w/\bar{M}_n = 2-2.2$; c) crystallinity (%): 76 (19), 85 (20), 90 (21); d) syndiotacticity (%): 93 (19), 94 (20), 95 (21); e) melting point (°C): 200 (19), 205 (20), 208 (21).

Table 3. Dependence of yield, molecular mass and microstructure of polybutadiene on concentration of reaction mixture components and polymerization temperature in the presence of nickel-containing catalytic dithiosystem - DEDTPh-Ni + DEAC (without preliminary formation of catalyst).

| Concentration of nickel compound, [Ni].10 ⁴ (mol/L) | Concentration of butadiene, [M], (mol/L) | Al:Ni | Temperature (°C) | Time (min) | Yield (% by mass) | Intrinsic viscosity, $[\eta]$ ₂₅ (dL/g) | Molecular mass, M.10 ⁻³ | | Microstructure (%) | | |
|--|--|-------|------------------|------------|-------------------|--|------------------------------------|-------------|--------------------|-----------|------|
| | | | | | | | \bar{M}_v | \bar{M}_n | 1,4-cis | 1,4-trans | 1,2- |
| 0.5 | 3 | 100 | 25 | 120 | 47 | 0.19 | 5.8 | 3.2 | 93 | 5 | 2 |
| 0.75 | 3 | 100 | 25 | 120 | 63 | 0.18 | 5.5 | 3.1 | 91 | 6 | 3 |
| 1 | 3 | 100 | 25 | 60 | 58 | 0.17 | 5.3 | 2.9 | 89 | 8 | 3 |
| 2.5 | 3 | 100 | 25 | 20 | 73 | 0.14 | 4.3 | 2.4 | 86 | 11 | 3 |
| 5 | 3 | 100 | 25 | 10 | 73 | 0.09 | 2.6 | 1.5 | 84 | 12 | 4 |
| 10 | 3 | 100 | 25 | 5 | 78 | 0.08 | 2.5 | 1.4 | 82 | 16 | 2 |
| 1 | 1.5 | 100 | 25 | 60 | 56 | 0.13 | 4.1 | 2.3 | 91 | 7 | 2 |
| 1 | 4.5 | 100 | 25 | 60 | 56 | 0.22 | 6.9 | 3.8 | 86 | 10 | 4 |
| 1 | 7 | 100 | 25 | 60 | 54 | 0.24 | 7.5 | 4.2 | 89 | 7 | 4 |
| 10 | 3 | 2 | 25 | 240 | 60 | 0.28 | 8.8 | 4.3 | 92 | 6 | 2 |
| 10 | 3 | 2.5 | 25 | 120 | 45 | 0.25 | 7.8 | 4.3 | 90 | 7 | 3 |
| 10 | 3 | 5 | 25 | 140 | 75 | 0.17 | 5.3 | 2.9 | 82 | 16 | 2 |
| 10 | 3 | 10 | 25 | 10 | 78 | 0.14 | 4.3 | 2.4 | 83 | 15 | 2 |
| 10 | 3 | 25 | 25 | 10 | 85 | 0.10 | 3.1 | 1.7 | 80 | 18 | 2 |
| 10 | 3 | 50 | 25 | 5 | 75 | 0.09 | 2.6 | 1.5 | 81 | 17 | 2 |
| 2.5 | 3 | 100 | 7 | 60 | 55 | 0.22 | 6.9 | 3.8 | 91 | 8 | 1 |
| 2.5 | 3 | 100 | 15 | 60 | 75 | 0.21 | 6.6 | 3.6 | 89 | 8 | 3 |
| 2.5 | 3 | 100 | 35 | 60 | 78 | 0.16 | 5.0 | 2.8 | 87 | 10 | 3 |
| 2.5 | 3 | 100 | 45 | 60 | 71 | 0.15 | 4.7 | 2.6 | 85 | 12 | 3 |
| 2.5 | 3 | 100 | 55 | 60 | 31 | 0.14 | 4.3 | 2.4 | 85 | 12 | 3 |

crystalline syndiotactic 1,2-PBD (1,2-SPBD) with intrinsic viscosity (135 C, tetralin) 2-3,1,2-content 93-99 %, crystallinity 63-98 % and mp 177-215 C [29].

On this basis the new catalysts and processes have been developed for the synthesis of low- and high molecular 1,4-cis- and high molecular cold resistant 1,4-cis + 1,2-polybutadiene, suitable for use in tyre industry.

As it is known 1,4-cis polybutadiene containing 30-40% of 1,2-units does not crystallize by cooling up to vitrification temperature that provides its high cold resistance. This polymer is a non-crystallizable statistical copolymer that is evidenced by thermograms of different samples presented in Figure 1.

The experimental data demonstrate that nickel- or

cobalt-containing catalytic dithiosystems are high activity and stereoselectivity catalysts for butadiene polymerization process. Varying the operating parameters (reaction conditions) such as catalyst components nature and concentrations, reaction temperature and order of addition of reaction components we can regulate activity and stereoselectivity of nickel- and cobalt-containing dithiosystems in a wide range (Tables 3-5).

The experimental results obtained allow us to establish the optimal parameters of synthesis:

Low-molecular (Liquid) 1,4-cis Polybutadiene [24-26]

Catalysts: Ni-DTPh, Ni-DTC or Ni-Xh+AAH; [Ni] = $5 \cdot 10^{-5}$ - $5 \cdot 10^{-4}$ mol/L; [M] = 1.5-6.0 mol/L Al: Ni = (10-100): 1; t = 15 - 45 C.

Table 4. Dependence of yield, molecular mass and microstructure of polybutadiene on concentration of reaction mixture components and temperature in the presence of cobalt-containing catalytic dithiosystems.

| Concentration of cobalt compound, [Co]. 10 ⁴ | Concentration of butadiene, [M] (mol/L) | Al:Ni | Temperature (°C) | Time (min) | Yield (% by mass) | Intrinsic viscosity, $[\eta]_{30}$ (dL/g) | Molecular mass, M.10 ⁻³ | | Microstructure (%) | | |
|---|---|-------|------------------|------------|-------------------|---|------------------------------------|-----------------|--------------------|-----------|------|
| | | | | | | | (\bar{M}_v) | (\bar{M}_n) | 1,4-cis | 1,4-trans | 1,2- |
| Catalytic system DEDTC-Co + DEAC | | | | | | | | | | | |
| 1 | 1.5 | 100 | 25 | 120 | 28 | 1.75 | 247 | 61 | 61 | 5 | 34 |
| 2.5 | 1.5 | 100 | 25 | 120 | 56 | 1.25 | 161 | 74 | 74 | 6 | 20 |
| 5 | 1.5 | 100 | 25 | 120 | 74 | 0.83 | 96 | 77 | 77 | 7 | 16 |
| 10 | 1.5 | 100 | 25 | 90 | 93 | 0.75 | 85 | 79 | 79 | 7 | 14 |
| 2.5 | 1.5 | 100 | 25 | 45 | 99 | 0.52 | 53 | 76 | 76 | 14 | 10 |
| 1 | 3.0 | 100 | 25 | 120 | 33 | 2.15 | 321 | - | 55 | 8 | 37 |
| 1 | 4.5 | 100 | 25 | 120 | 29 | 2.95 | 478 | - | 63 | 5 | 32 |
| 1 | 6.0 | 100 | 25 | 120 | 27 | 3.65 | 627 | - | 54 | 7 | 39 |
| 10 | 1.5 | 10 | 25 | 90 | 7 | 2.50 | 388 | - | 57 | 9 | 34 |
| 10 | 1.5 | 17 | 25 | 90 | 30 | 1.90 | 274 | - | 60 | 9 | 31 |
| 10 | 1.5 | 25 | 25 | 90 | 30 | 1.50 | 203 | - | 60 | 9 | 31 |
| 10 | 1.5 | 50 | 25 | 90 | 57 | 1.40 | 186 | - | 74 | 9 | 17 |
| 10 | 1.5 | 250 | 25 | 90 | 78 | 0.75 | 85 | - | 76 | 10 | 14 |
| 10 | 1.5 | 500 | 25 | 90 | 93 | 0.15 | 11 | - | 79 | 9 | 12 |
| 1 | 1.5 | 100 | 15 | 120 | 15 | 2.15 | 321 | - | 63 | 0 | 37 |
| 1 | 1.5 | 100 | 35 | 120 | 26 | 0.85 | 99 | - | 75 | 9 | 16 |
| 1 | 1.5 | 100 | 45 | 120 | 24 | 0.35 | 32 | - | 77 | 9 | 14 |
| 1 | 1.5 | 100 | 55 | 120 | 26 | 0.30 | 26 | - | 71 | 7 | 22 |
| 1 | 1.5 | 100 | 65 | 120 | 20 | 0.15 | 11 | - | 65 | 9 | 26 |
| Catalytic system DiPDTPH-Co + DEAC | | | | | | | | | | | |
| 2.5 | 3.0 | 100 | 25 | 60 | 88 | 1.46 | 120 | 66 | 94 | 4 | 2 |
| 5.0 | 3.0 | 100 | 25 | 20 | 75 | 1.38 | 110 | 61 | 91 | 6 | 3 |
| 7.5 | 3.0 | 100 | 25 | 15 | 80 | 1.34 | 106 | 59 | 91 | 7 | 2 |
| 10.0 | 3.0 | 100 | 25 | 10 | 74 | 1.32 | 100 | 55 | 88 | 9 | 3 |
| 2.5 | 3.0 | 100 | 25 | 15 | 85 | 1.04 | 75 | 42 | 86 | 10 | 4 |
| 2.5 | 1.5 | 100 | 25 | 60 | 85 | 1.07 | 78 | 43 | 90 | 7 | 3 |
| 2.5 | 4.5 | 100 | 25 | 60 | 78 | 1.57 | 132 | 73 | 96 | 2 | 2 |
| 2.5 | 7.0 | 100 | 25 | 60 | 82 | 1.92 | 170 | 94 | 97 | 2 | 1 |
| 2.5 | 3.0 | 10 | 25 | 120 | 15 | 1.55 | 130 | 70 | 95 | 3 | 2 |
| 2.5 | 3.0 | 50 | 25 | 60 | 70 | 1.50 | 125 | 69 | 94 | 5 | 1 |
| 2.5 | 3.0 | 200 | 25 | 15 | 85 | 1.40 | 120 | 63 | 92 | 6 | 2 |
| 2.5 | 3.0 | 100 | 15 | 150 | 58 | 1.52 | 140 | 75 | 96 | 3 | 1 |
| 2.5 | 3.0 | 100 | 35 | 50 | 96 | 1.42 | 125 | 64 | 93 | 5 | 2 |
| 2.5 | 3.0 | 100 | 45 | 15 | 89 | 1.38 | 105 | 62 | 88 | 8 | 4 |

High-molecular 1,4-cis Polybutadiene [27]

Catalysts: Co-DTPH+AAH; [Co] = 2.5×10^{-5} - 5.0×10^{-4} mol/L; [M] = 1.5-3.0 mol/L; Al:Co = (10-200): 1; t = 15 - 45 C.

High-molecular 1,4-cis + 1,2-Polybutadiene [27]

Catalysts: Co-DTC+AAH; [Co] = 1.0×10^{-4} - 2.5×10^{-4} mol/L; [M] = 1.5 - 3.0 mol/L; Al:Co = (10-100): 1; t = 25 - 45 C.

High-molecular and Highly Crystalline Syndiotactic 1,2-Polybutadiene [24]

Catalysts: Co-Xh+TAA; [Co] = 1.0×10^{-4} - 1.0×10^{-3} mol/L; [M] = 1.5 - 3.0 mol/L; Al:Co = (10-100): 1; t = 10 - 80 C.

High activities of the newly-developed catalytic dithiosystems allow us the use of a raw material, not only pure butadiene, but also butadiene in C₄ pyrolysis fraction.

Nickel- and cobalt-containing catalytic dithiosystems and processes for production of various types of polybutadienes were tested starting from laboratory continuous unit to semi-industry plant and are ready for industrial applications.

Development of the technological aspects of different types butadiene rubbers production using the new highly-active catalytic dithiosystems will allow organizing the ecologically favourable stereoregular polybutadienes preparation processes.

Despite of the copious scientific literature, the mechanism of butadiene polymerization by cobalt and nickel-based co-ordination catalysts has not been fully elucidated. The complexity of the catalyst and feedstock and the difficulty of controlling the system properly have meant that a unified mechanism is still not at hand.

The study of the kinetic rules of butadiene polymerization process in the presence of nickel-containing catalytic dithiosystem DEDTPH-Ni+DEAC showed that both without preliminary catalyst formation and with preliminary catalyst formation the polymerization rate was proportional to the concentrations of nickel and butadiene compounds to a first-order. With Al: Ni ratios in the range of 2:1 to 10:1 the polymerization order by aluminium approaches to two and at further increase of these values in the range of (10-250):1 the decrease of this dependence is observed down to its

complete absence [24, 30, 31].

The temperature effect on polymerization kinetics without preliminary catalyst formation has an extreme nature [24, 30]. The temperature rise from 15 C to 25 C leads to the increase of polymerization rate. Within 25-45 C the process rate at the initial stages is practically independent of temperature but in this case the initial induction period disappears. Further, the temperature rise leads to the rate drop. Taking this into consideration on the curves of polymerization rate dependence in Arrhenius equation co-ordinates three sections of temperature changes of polymerization rate are distinguished:

- Section with observed positive activation energy ($E_{act} > 0$);
- Section with $E_{act} = 0$;
- Section with observed negative activation energy ($E_{act} < 0$).

The activation energies values calculated in the first and third sections amount to 41.8 kJ/mol and -98.2 kJ/mol, respectively.

In contrast to this, in preliminary catalyst formation with temperature rise from 15 C to 55 C the polymerization rate increases and activation energy value is 43.9 kJ/mol.

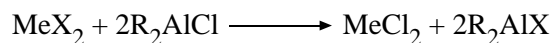
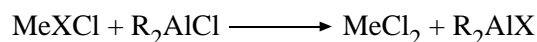
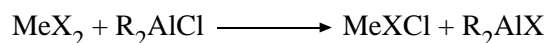
The detailed investigations of the butadiene polymerization kinetic rules in the presence of cobalt dithiophosphate (DiPDTPh-Co+DEAC) and cobalt dithiocarbamate (DEDTC-Co+DEAC) systems showed that they are identical with the rules found early for the nickel-containing dithiosystems: in this case the first-order with respect to cobalt and butadiene compounds involves and the order with respect to aluminium changes from 2 to 0 [24, 32].

The activation energy values determined are 39.4 kJ/mol for cobalt dithiophosphate catalytic system and 38.3 kJ/mol for cobalt dithiocarbamate system.

As a result of butadiene polymerization kinetic rules study in the presence of nickel- and cobalt containing dithiosystems, there have been established main elementary stages of the process: exchange of acydo-ligands, alkylation, chain growth, transfer to monomer, bimolecular deactivation, redox restriction with organoaluminium compound participation.

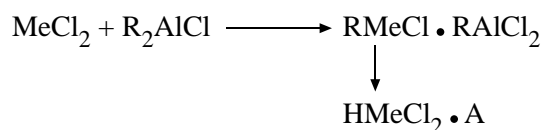
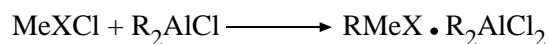
These reactions scheme are given below:

1. Exchange reaction



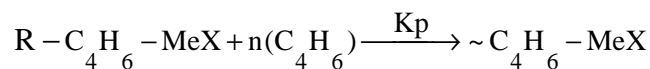
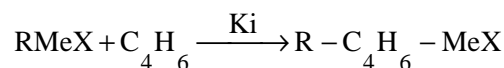
wherein, X-dithio group, Me- transition metal atom.

2. Alkylation



wherein, A- organoaluminium compound molecule.

3. Growth centres formation and chain growth



4. Chain transfer to monomer

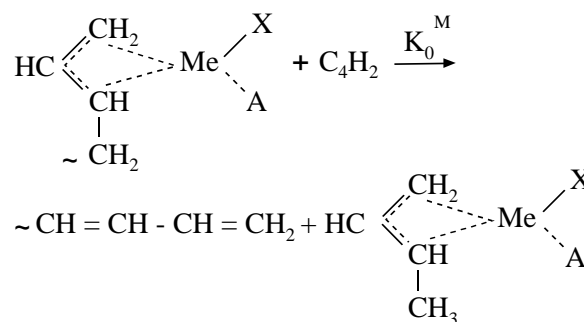
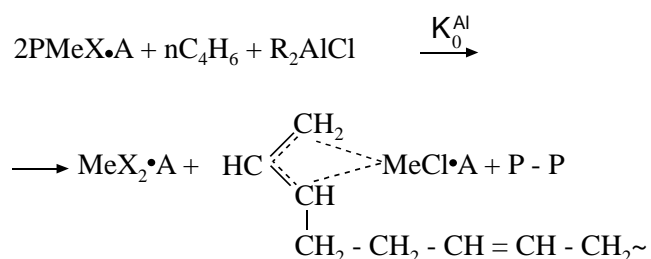
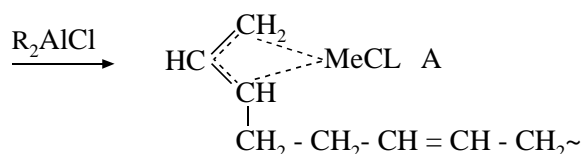
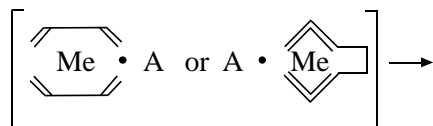
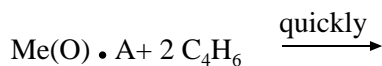
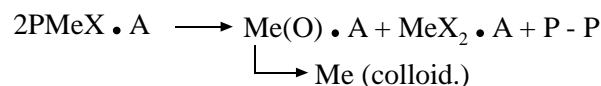


Table 5. Dependence of yield, molecular mass and microstructure of polybutadiene on concentration of reaction mixture components and temperature in the presence of cobalt xanthogenate catalytic dithiosystem $i\text{PrX-Co} + \text{TEA}$

| Concentration of cobalt compound, [Co], 10^4 | Concentration of butadiene, [M] (mol/L) | Al:Ni | Temperature ($^{\circ}\text{C}$) | Time (min) | Yield (% by mass) | Intrinsic viscosity (in tetralin), $[\eta]_{135}$ (dL/g) | Crystallinity (%) | Syndiotacticity (%) | Melting point ($^{\circ}\text{C}$) | Microstructure (%) | | |
|--|---|-------|------------------------------------|------------|-------------------|--|-------------------|---------------------|--------------------------------------|--------------------|-----------|------|
| | | | | | | | | | | 1,4-cis | 1,4-trans | 1,2- |
| 0.2 | 3.0 | 100 | 40 | 180 | 30 | 3.0 | 68 | 94 | 212 | 1 | - | 99 |
| 0.5 | 3.0 | 100 | 40 | 120 | 65 | 2.8 | 72 | 94 | 212 | 1 | - | 99 |
| 1.0 | 3.0 | 100 | 40 | 90 | 85 | 2.5 | 76 | 95 | 210 | 1 | 1 | 98 |
| 2.0 | 3.0 | 100 | 40 | 60 | 98 | 2.3 | 85 | 94 | 205 | 1 | 1 | 98 |
| 5.0 | 3.0 | 100 | 40 | 15 | 99 | 2.1 | 90 | 97 | 197 | 2 | 1 | 97 |
| 10.0 | 3.0 | 100 | 40 | 5 | 97 | 1.7 | 95 | 96 | 187 | 3 | 2 | 95 |
| 2.0 | 1.5 | 100 | 40 | 60 | 97 | 2.0 | 84 | 95 | 207 | 2 | 1 | 97 |
| 2.0 | 6.0 | 100 | 40 | 45 | 90 | 3.2 | 87 | 98 | 203 | 1 | - | 99 |
| 2.0 | 3.0 | 10 | 40 | 180 | 65 | 2.9 | 70 | 94 | 208 | 1 | - | 99 |
| 2.0 | 3.0 | 25 | 40 | 90 | 83 | 2.7 | 73 | 94 | 206 | 1 | - | 99 |
| 2.0 | 3.0 | 50 | 40 | 60 | 91 | 2.4 | 78 | 95 | 206 | 1 | 1 | 98 |
| 2.0 | 3.0 | 150 | 40 | 45 | 99 | 2.0 | 96 | 97 | 203 | 3 | 1 | 96 |
| 2.0 | 3.0 | 200 | 40 | 30 | 98 | 1.5 | 96 | 96 | 202 | 4 | 2 | 94 |
| 2.0 | 3.0 | 100 | 0 | 180 | 26 | 3.5 | 98 | 93 | 215 | 1 | - | 99 |
| 2.0 | 3.0 | 100 | 10 | 120 | 45 | 2.8 | 93 | 93 | 212 | 1 | - | 98 |
| 2.0 | 3.0 | 100 | 25 | 60 | 95 | 2.4 | 90 | 94 | 209 | 1 | 1 | 97 |
| 2.0 | 3.0 | 100 | 55 | 45 | 98 | 2.0 | 81 | 95 | 194 | 4 | 1 | 95 |
| 2.0 | 3.0 | 100 | 80 | 45 | 99 | 1.5 | 68 | 96 | 180 | 4 | 2 | 94 |
| 2.0 | 3.0 | 100 | 100 | 45 | 99 | 1.3 | 63 | 95 | 177 | 5 | 1 | 94 |

5. Bimolecular deactivation and redox restriction with organoaluminium compound participation.



wherein, P is a growing chain.

Taking into account the established elementary stages there have been derived the following equations:

- for the polymerization total rate

$$V_{\text{pol}} = K_p^{\text{cf}} \cdot [\text{M}] \frac{[\text{Me}]_0 - [\text{Me}]_0 \cdot e^{-K_\alpha[\text{Al}]^l \cdot \tau}}{1 + K_D \cdot \tau([\text{Me}]_0 - [\text{Me}]_0 \cdot e^{-K_\alpha[\text{Al}]^l \cdot \tau})} \quad (1)$$

- for monomer consumption in descending branch of the kinetic curves rate-time

$$\log \frac{M_z}{M_\tau} = \frac{K_p}{K_D} \cdot \log[1 + K_D \cdot n_p^{\text{max}} \cdot (\tau - \tau_{\text{max}})] \quad (2)$$

- and, for degree of polymerization at monomer high conversions

$$\frac{1}{P_{\text{pol}}} = \frac{K_o^{\text{M}}}{K_p} + \frac{K_o^{\text{Al}}}{K_p \cdot [\text{M}]} [\text{Al}]^l \cdot [\text{Me}]_0 \quad (3)$$

wherein, $[\text{Me}]_0$, $[\text{M}]$, $[\text{Al}]$ are concentrations of nickel or cobalt, monomer and aluminium, respectively; n_p^{max}

is maximum concentration of the growth centers, and l is order of redox restriction by aluminium.

These equations explain well the experimental data and allow us to calculate the values of the elementary studies kinetic parameters (K_a - total rate constant of potential centers formation; K_p - growth rate constant; K_D - bimolecular deactivation rate constant; K_o^{M} - rate constant of transfer to monomer; E_a , E_p , E_d - activation energies of the corresponding stages; V_d , V_o^{M} , V_p - initial rates of elementary stages) with the help of computer. The results of calculation are set in Table 6. As it is noticed in Table 6, the maximum concentration of the growth centres is:

- 13-44 % for nickel-containing dithiosystem,
- 21-57 % for cobalt dithiophosphate system,
- 19-68 % for cobalt dithiocarbamate system.

The analysis of the found values of the kinetic parameters shows that the process of growth restriction on dithiosystem and the restriction with organoaluminium compound participation as well as a transfer to monomer are inessential. Under the experiment conditions the obtained rates of bimolecular deactivation of growth centres, redox restriction with organoaluminium compound participation and transfer to monomer are comparable (though for nickel-containing dithiosystem V_d is well larger than V_o^{M} and V_o^{Al} , and E_d surpasses E_p by 19.2 kJ/mol).

However, the role of these reactions is not so great as their rates have the order 10^{-6} - 10^{-7} mol/L x min, while time rate of chain growth has the order 10^{-1} - 10^{-3} mol/L x min. Just, such ratio of the elementary stages rates provides the preparation of relatively high-molecular 1,4-cis polybutadiene on cobalt dithiophosphate and 1,4-cis+1,2-polybutadiene on cobalt dithiocarbamate catalytic systems in contrast to the nickel-containing dithiosystems providing the preparation of very low-molecular 1,4-cis polybutadiene.

Catalytic systems of Ziegler-Natta type, containing Ni-DTC or Ni-DTPH and DEAC, lead to formation of low-molecular polybutadiene ($\overline{M}_n = 10^3$ - 10^4). In this case 1,4-cis-units content ranges within 70-90 %; the lesser polybutadiene molecular mass the more 1,4-trans-units in it. The increase of Ni and Al compounds concentration, butadiene concentration as well as the increase of aluminium-organic compound complexing ability in passing from monochloride to dichloride favour a decrease of molecular masses (MM) and

Table 6. Comparison of kinetic parameters of butadiene polymerization process in the presence of nickel- and cobalt-containing catalytic dithiosystems. Polymerization conditions: [Ni]= 2.5×10^{-4} mol/L, [M]= 3.0 mol/L, Al: Ni= 100:1; [Co]= $1.10 \cdot 10^{-4}$ mol/L, [M]=1.5 mol/L, Al: Co= 100:1, solvent is toluene.

| Polymerization temperature (°C) | Maximal concentr. of growth centres, η_p^{\max} | Rate constants of stages | | | | | Activation energies of stages | | | Initial rates of elementary stages | | | |
|---------------------------------|--|--|----------------|----------------|-----------------------------|------------------------------|-------------------------------|----------------|----------------|------------------------------------|-----------------------------|------------------------------|----------------|
| | | (L ² / mol ² .min) | | | (L/mol.min) | | kJ/mol | | | V.10 ⁶ (mol/L.min) | | | |
| | | K _a | K _p | K _d | K _o ^M | K _o ^{Al} | E _a | E _p | E _d | V _d | V _o ^M | V _o ^{Al} | V _p |
| Nickel-containing dithiosystem | | | | | | | | | | | | | |
| 15 | 44 | 67 | 437 | 349 | | | | | | | | | |
| 25 | 36 | 91 | 898 | 1076 | | | | | | 4.22 | | | 144200 |
| 35 | 28 | 183 | 967 | 1376 | 12 | 11 | 34.3 | 30.5 | 49.7 | 8.72 | | | 242460 |
| 45 | 20 | 239 | 1415 | 3028 | | | | | | 6.74 | 0.324 | 0.1 | 203060 |
| 55 | 13 | - | 2538 | 4220 | | | | | | 7.57 | | | 212250 |
| | | | | | | | | | | 4.46 | | | 247455 |
| Cobalt dithiophosphate system | | | | | | | | | | | | | |
| 15 | 23 | 25 | 6 | 76 | $3.3 \cdot 10^{-4}$ | | | | | 0.18 | 0.0076 | | 138 |
| 25 | 57 | 53.3 | 15 | 138 | $8.2 \cdot 10^{-4}$ | | | | | 0.45 | 0.0232 | | 1283 |
| 35 | 38 | 105.5 | 26 | 270 | $1.4 \cdot 10^{-3}$ | $8.3 \cdot 10^{-3}$ | 49.5 | 32.3 | 38.6 | 0.38 | 0.08 | 0.19 | 1483 |
| 45 | 21 | 210 | 33 | 418 | $1.8 \cdot 10^{-3}$ | | | | | 0.18 | 0.057 | | 1040 |
| Cobalt dithiocarbamate system | | | | | | | | | | | | | |
| 15 | 27 | 30 | 8 | 81 | 0.00133 | 0.014 | | | | 0.06 | 0.054 | 0.378 | 324 |
| 25 | 68 | 64 | 15 | 147 | 0.0031 | 0.091 | | | | 0.68 | 0.316 | 6.19 | 1530 |
| 35 | 40 | 127 | 23 | 256 | 0.0122 | 0.937 | 52.3 | 35.6 | 42.6 | 0.41 | 0.762 | 37.48 | 1380 |
| 45 | 26 | 240 | 35 | 433 | 0.059 | 1.267 | | | | 0.293 | 2.301 | 32.94 | 1370 |
| 55 | 19 | 437 | 51 | 708 | 0.102 | 0.22 | | | | 0.256 | 2.91 | 4.18 | 1450 |

increase of 1,4-trans-units.

It should be noted that in numerous studies of different authors (Dolgoplosk B.A., Tinyakova Y.I. et al.) [1], it was formerly established that the introduction to cis-regulating systems of strong electron donors of triphenyl phosphine, dibutyl sulphide, tetrahydrofuran causes, as a rule, decrease of both activity and stereospecificity: 1,4-trans-units content increases in polybutadiene. However, it is hardly able to assign a decrease of stereospecificity and molecular masses values in the case of dithiosystems to electron donor effect of dithio group as these systems by its activity considerably (by two orders) exceed -alkenyl systems though lead to formation of polybutadiene with low molecular mass.

The studies we carried out showed that the high activity of dithiosystems is due to the presence in these systems of polar catalytic centers containing

dithiogroup.

The dithiosystems are not the only catalysts of butadiene cis-polymerization by means of which the interrelation between molecular mass and microstructure of polybutadiene is traced. Similarity in changes of molecular mass and 1,4-cis-units content it is found out also from data analysis of different systems catalytic effect which are listed in Table 7. As it is seen, the larger ligands favour MM decrease with the lower cis-units content.

We found similar rules in series of 1,4-regulating cobalt-containing dithiosystems as well.

However, higher complex pattern is observed in the case of systems providing the formation of polybutadiene of mixed 1,4- + 1,2-structures. Thus, for example, decrease of molecular mass on catalytic system DEDTC-Co + DEAC is accompanied by the decrease

Table 7. Interrelation between MM and microstructure of polybutadiene prepared from different nickel-containing catalytic systems.

| Catalytic system | $[\eta]_{25}$ (dL/g) | Microstructure (%) | | |
|---|----------------------|--------------------|-----------|------|
| | | 1,4-cis | 1,4-trans | 1,2- |
| Ni (BF ₄) ₂ ·6(i-C ₄ H ₉ OH) + (i-C ₄ H ₉) ₃ Al + CF ₃ COOH | 7.0 | 99.6 | 0.2 | 0.2 |
| NiSiF ₆ ·6C ₂ H ₅ OH + (C ₂ H ₅) ₃ Al | 3.7 | 98.6 | 0.1 | 0.3 |
| Ni (naphthenate) ₂ + (C ₂ H ₅) ₃ Al + H ₂ O + C ₆ H ₅ CF ₃ + CCl ₃ COOH | 3.38 | 97.0 | 1.5 | 1.5 |
| Ni (octanate) ₂ + (C ₂ H ₅) ₃ Al + BF ₃ ·(C ₂ H ₅) ₂ O + 1,4-cis-polybutadiene | 2.86 | 97.0 | 1.5 | 1.5 |
| (π -C ₄ H ₇ NiCl) ₂ + Chloranyl | 1.70 | 97.0 | 2.0 | 1.0 |
| Ni (naphthenate) ₂ + (C ₂ H ₅) ₂ AlF + CCl ₃ COOH | 1.35 | 93.2 | 4.0 | 2.8 |
| (π -C ₃ H ₅ NiCl) ₂ + TiCl ₄ | 1.13 | 95.1 | 3.7 | 1.2 |
| (π -C ₅ H ₉ NiCl) ₂ + TiCl ₄ | 1.08 | 91.6 | 6.5 | 1.9 |
| DEDTC-Ni + (C ₂ H ₅) ₂ Al | 0.17 | 89.0 | 8.0 | 3.0 |
| Ni (stearate) ₂ + (C ₂ H ₅) ₂ AlCl | 0.115 | 78.0 | 20.0 | 2.0 |
| Ni (naphthenate) ₂ + (C ₂ H ₅) ₃ Al ₂ Cl ₃ | 0.09 | 72.0 | 26.0 | 2.0 |

of 1,4-units total content. By this the given system differs from many cobalt systems in the presence of which MM decrease is accompanied by 1,2-units content increase.

The analysis of our published literature data [32] showed that in cobalt systems in general there are observe different variants of interrelated changes of polybutadiene molecular masses and microstructure. It has been concluded that on the same metal, depending on degree of its oxidation as well as on ligand nature and reaction medium, the polydienes with various combinations of MM and microstructure may be produced (Table 8).

On this basis the new cobalt-containing catalysts have been developed for the synthesis of high-molecular 1,4-cis-polybutadiene suitable for use in tyre industry.

Using cobalt dithiocarbamate system the high-molecular cold resistant 1,4-cis+1,2-polybutadiene has been produced with 35-37 % of 1,2-units. This polymer is non-crystallizable statistical copolymer that is evidenced by thermograms of different samples presented in Figure 1.

The other important result was obtained by study of polymer microstructure dependence on its fractional composition. It was proved that with increase of polybutadiene separate fractions in molecular mass (polybutadiene was prepared in the presence of cis-regulating systems) the share of cis-units in polymer rises. Very high-molecular polybutadiene consists almost

exceptionally of 1,4-cis-units [30].

The complex of the obtained results allowed proposing the following scheme of interrelated molecular mass and stereoregulating in polybutadiene synthesis (Scheme I).

The proposed Scheme I is based on the known ideas of Dolgoplosk B.A. et al. [1] on the role of *syn-*

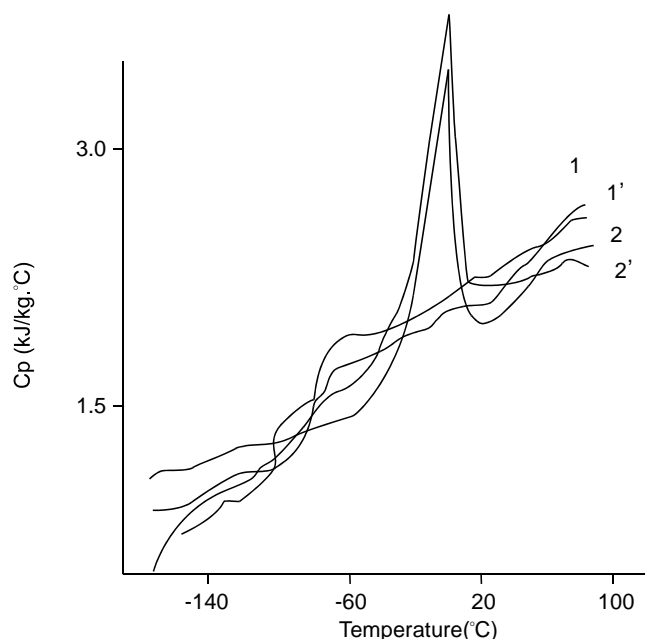
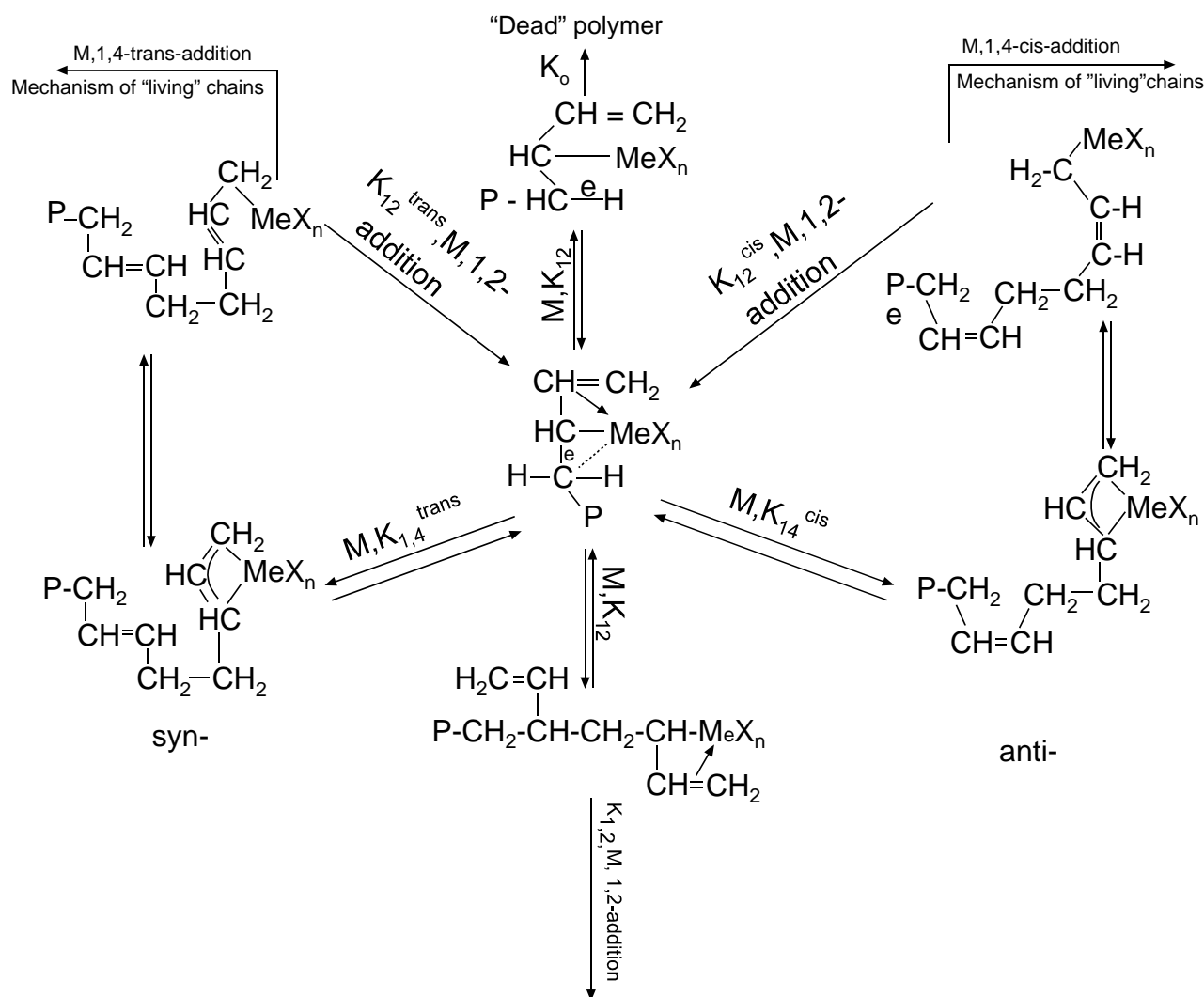


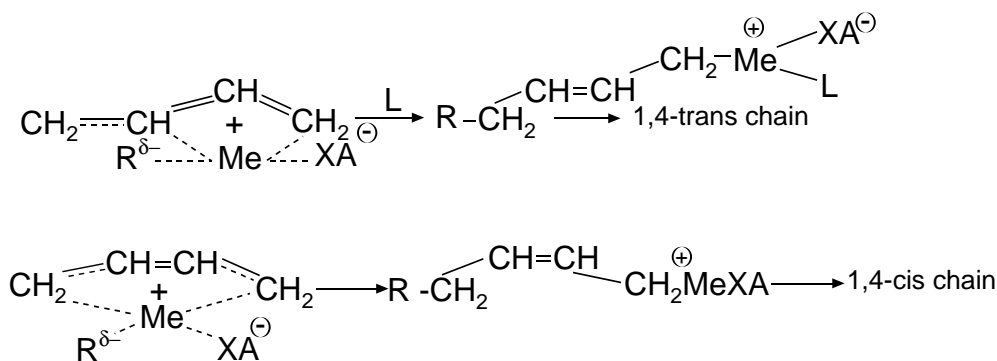
Figure 1. Thermograms of different PBD samples, obtained on cobalt containing catalytic dithiosystems: 1,2-starting and 1',2'-after annealing samples of PBD; Microstructure: 1-57% 1,4-cis; 6% 1,4-trans; 37% 1,2; 2-95% 1,4-cis; 3% 1,4-trans; 2% 1,2.



anti isomerization and method of monomer co-ordination in intermediate organometallic centres in stereo-regulating in diene polymerization process. Its distinctive feature is the accounting the role of β_{CH} agostic interaction as a factor of chain growth limitation proposed by Azizov A.H. and us in [24, 33]. Besides, the attention should be distinctively emphasized on still one moment concerning stereoregulating mechanism. The question is about the role of η^3 -co-ordination of butadiene in intermediate metallinium-ion complexes. It is supposed that this complex subsequent rearrangement to *syn*- η^3 -alkenyl or η^1 -1,4-*trans*-alkenyl organometallic derivative fixes the end unit in *trans*-configuration. In contrast to η^3 -co-ordination η^4 -co-ordination leads to *anti*- η^3 -alkenyl organometallic derivative and, respectively, to 1,4-*cis*-structure of end unit (Scheme II).

Electronic and steric effects and ligand quantitative composition in metal co-ordination sphere control the possibilities of realization of that or another method of co-ordination in the first place. For η^4 -co-ordination the larger co-ordination unsaturation and more favourable steric conditions than for η^3 -co-ordination are necessary.

1,2-Structure of unit, probably, is formed mainly after 2-co-ordination with subsequent formation of η^1 or η^1, η^2 -organometallic complex. The results of study of regioselectivity and isomerization processes give reasons to state that butadiene η^2 -co-ordination may be completed both M-C₁- and M-C₂-addition. The first direction leads to formation of β_{CH} -agostic η^1 -derivative and five-chelated η^1, η^2 -derivative. M-C₂-derivative completes by formation of four-chelated η^1, η^2 -derivative (Scheme III).



Scheme II

Chain restriction occurs basically in agostic η^1 -complex. Sufficiently convincing confirmation of it is the fact of introducing butene-1 molecules to chain as end unit in co-oligomerization model reaction with butadiene. β_{CH} -agostic interacting makes easier as in co-oligomerization restriction of chain growth by mechanism of β_{CH} -hydrogen separation or transfer.

Blocking of β_{CH} -agostic interaction at the expense of $d\pi, \pi\pi$ -interaction with double bond to η^1, η^2 -complexes increases kinetic stability of end unit and thereby favours η^1, η^2 -growth of chain.

In 1,4-addition of end unit there is no possibility for β_{CH} -agostic interaction of all and, accordingly, chain growth is affected by mechanism of living chains. It is this reason that high-molecular polybutadiene is characterized by high stereoregulation.

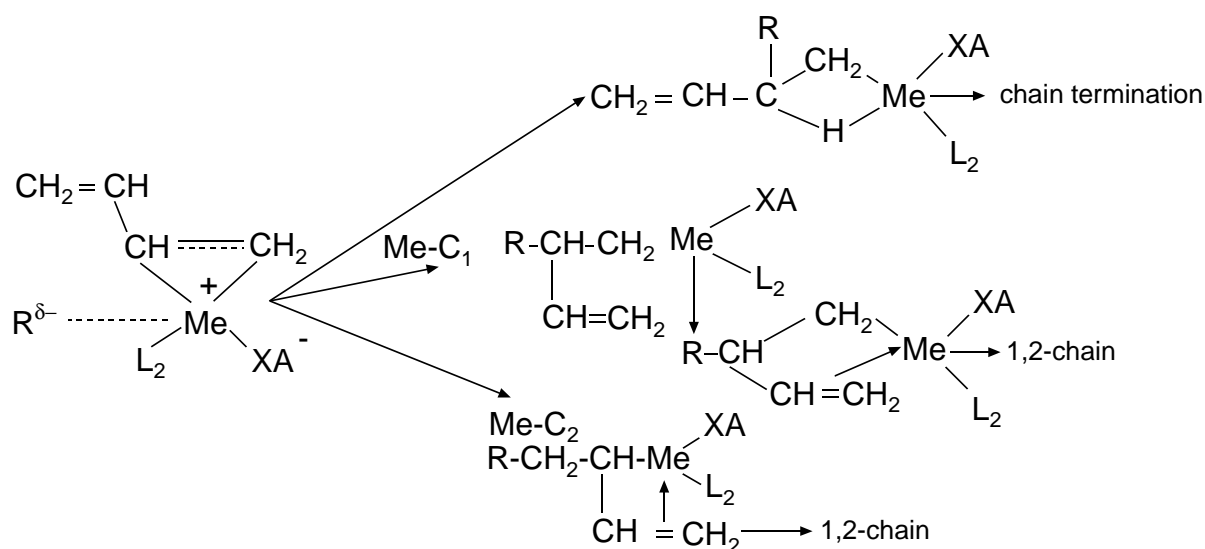
Hence, in butadiene polymerization the chain growth is actually affected not on kinetic non-stable σ -

or sufficiently stable π -alkenyl centers but with participation of mobile η^1, η^2 -chelated co-ordination-unsaturated centres.

It has been shown that preparation of polymer with mixed structure (1,4-cis + 1,4-trans + 1,2) is the result of metal co-ordination sphere changes in the course of polymerization. In this respect it is significant by different nature of changes of polybutadiene microstructure produced on nickel- and cobalt-containing dithiosystems depending on time: on nickel system with increasing reaction time (conversion) increases 1,4-trans units and on cobalt system increases 1,4-cis units.

The co-ordination sphere change is also shown in dependence of polymerization time profile on catalyst preparation conditions and reaction proceeds: the kinetic curves shape changes from an S shape to sloping.

Hence, to achieve high stereospecificity relative to forming this or other microstructure it is necessary, first



Scheme III

Table 8. Experimentally observed variants of interrelation between MM and microstructure of PBD prepared on cobalt-containing catalytic systems.

| Variants | Catalytic system | $[\eta]_{25}$, dL/g | Microstructure (%) | | |
|---|--|------------------------|---------------------|---------------------|---------------------|
| | | | 1,4-cis | 1,4-trans | 1,2- |
| Preparation of very high-molecular PBD with high content of 1,4-cis-links | $\text{CoCl}_2 \cdot \text{Py} + \text{R}_2\text{AlCl} + \text{H}_2\text{O}$ | 6.2 \rightarrow 4.0 | 98 \rightarrow 96 | 1 \rightarrow 3 | 1 |
| Preparation of very high-molecular PBD with high content of 1,4-trans-links | CoCl_2 (or soluble cobaltous salts) + $\text{R}_3\text{AlCl} + \text{NR}_3$ | — | — | 94 | 6 |
| Preparation of very high-molecular PBD with high content of 1,2-links | Cobaltous salts (carboxylates, acac.) + $\text{R}_3\text{AlX} +$ + alkyl lithium + CS_2 | 5.0 | 1 | — | 99 |
| Preparation of 1,4-cis + 1,2-PBD: -MM decrease is accompanied by decrease of 1,2-links content and by increase of 1,4-cis-links -MM decrease is accompanied by increase of 1,2-links content and by decrease of 1,4-cis-links | $\text{Co} [\text{R}_2\text{NC}(\text{S})\text{S}]_2 + \text{R}_2\text{AlCl}$ | 2.9 \rightarrow 0.12 | 64 \rightarrow 80 | 1 \rightarrow 5 | 35 \rightarrow 10 |
| | $\text{Co} [\text{R}^1\text{R}^2\text{NC}(\text{S})\text{S}]_n + \text{R}_n\text{AlCl}_{3-n} + \text{H}_2\text{O}$ | 10 \rightarrow 1 | 50 \rightarrow 91 | 2 | 50 \rightarrow 7 |
| | $\text{CoCl}_2 + \text{R}_2\text{AlCl} + \text{H}_2\text{O} + \text{R}_3\text{Al}$ (or electron donor) | 3.0 \rightarrow 0.4 | 92 \rightarrow 49 | 2 \rightarrow 6 | 4 \rightarrow 45 |
| Preparation of 1,4-cis + 1,4-trans-PBD: -MM decrease is accompanied by decrease of 1,4-trans-links content and by increase of 1,4-cis-links -MM decrease is accompanied by increase of 1,4-trans-links content and by decrease of 1,4-cis-links | $\text{Co} (\text{acac})_2 + (\text{C}_2\text{H}_5)_3\text{Al}$ | 0.5 \rightarrow 0.3 | 93 \rightarrow 97 | 6 \rightarrow 1 | 1 \rightarrow 2 |
| | $\text{CoCl}_2 \cdot 4\text{C}_2\text{H}_5\text{OH} + \text{R}_2\text{AlCl}$ | 6 \rightarrow 3.5 | 97 \rightarrow 90 | 2 \rightarrow 9 | 1 |
| | $\text{Co} (\text{stearate})_2 + (\text{i-C}_4\text{H}_9)_3\text{Al}$ | — | 8 | 22 | 70 |
| Preparation of 1,2 + 1,4-trans-PBD: -MM decrease is accompanied by decrease of 1,2-links content and by increase of 1,4-trans-links -MM decrease is accompanied by increase of 1,2-links content and by decrease of 1,4-trans-links | Cobaltous salts (acac., carboxylates) + $\text{R}_2\text{AlCl} + \text{NR}_3 +$ Methanol | — | — | 95 \rightarrow 72 | 5 \rightarrow 28 |
| | | | | | |
| Preparation of 1,4-cis + 1,4-trans + 1,2-PBD | $\text{CoCl}_2 + \text{AlR}_3$ (1:5) | — | 24 | 19 | 57 |
| | $\text{Co} (\text{benzoate})_2 + (\text{C}_2\text{H}_5)_2\text{AlCl}$ | — | 71 | 12 | 17 |

of all, to provide preservation of transition metal co-ordination sphere constancy during chain growth.

In the proposed scheme the other ways of restriction have not been taken into account, in particular, chain transfer to organoaluminium compound, mono- and bimolecular kinetic termination and other. Non-accounting of these factors is based on the results of kinetic studies, which show that the share of chain growth restriction processes effecting by means of hydrogen transfer (β -elimination, transfer to monomer) in the most cases prevails over the rest. Moreover, as we have established in [24, 34, 35], the role of organoaluminium compounds as regulator of MM consists not only in exchange of aluminium alkyl radicals for growing chain, as it is generally accepted, but in intensification of redox and chain spontaneous termination processes going with participation of organoaluminium compounds. However, the share of these processes is also insignificant.

CONCLUSION

- The new high activity and stereoselectivity catalytic systems for butadiene polymerization process have been developed. Based on Ni- and Co-dithioderivatives in combination with aluminium organic compounds (nickel- and cobalt-dithiosystems) they provide the preparation of low- and high-molecular 1,4-cis-, high-molecular 1,4-cis + 1,2- and syndiotactic 1,2-polybutadienes.

- The main feature of these systems is: high catalytic activity and stereoselectivity; decreasing the amount of metal complex component (almost by one order); sharply increasing the output of the product amount (by 4-5 times); using the butadiene fraction with low content of basic substance (fraction C_4) in the process.

- The study of kinetic rules of butadiene polymerization process in the presence of nickel- and cobalt containing catalytic dithiosystems showed that the polymerization rate was proportional to the concentrations of Ni or Co and butadiene compounds according to the first - order, and Al compound - from 2 to 0.

- The main elementary stages of the butadiene polymerization process have been established: exchange of acidoligands, alkylation, chain growth, transfer to

monomer, bimolecular deactivation and redox restriction with organ aluminium compound participation.

- The main factor responsible for 1,4-regulation of polybutadiene microstructure in the course of synthesis is not only *anti-syn*-isomerization in the end π -alkenyl fragments of the growing chain, but also the method of monomer co-ordination and, accordingly, the fastening of link in cis-, trans- or 1,2-forms.

- Limitation of the chain growth by the mechanism of β -hydrogen transfer (or elimination) occurs mainly at 1,2-addition of the end link but not at 1,4-addition.

- For preparation of polybutadiene with optimal stereoregularity not only the transition metal nature catalysts is a determining factor. Very important is also the optimal combination of metal oxidation degree with the ligands electronic and steric effects and their quantitative ratio in a co-ordination sphere (effects of quantitative and qualitative ligand control).

- The optimal regulation of the molecular mass of polymer stereoregularity and catalyst activity is possible in such systems where the largest values of molecular masses and stereoregularity to 1,4-cis- links formation are achieved.

- In these systems, by ligand control a necessary degree of stereoregularity can be achieved, not below the lower limits of the molecular masses values required for practical utilization.

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SYMBOLS AND ABBREVIATIONS

4-m,6-TBPh-Co = Cobalt 2,2'-thio-bis-O,O-di-4-methyl-6-*tert*.butylphenyl dithiophosphate
AAH = Alkylaluminiumhalide

Bu = Butyl
 Co = Cobalt
 CS₂ = Carbon disulphide
 CTPH-Co = Cobalt *O,O'*-di-4-methylphenyl dithiophosphate
 DAAC = Dialkylaluminiumchloride
 DEAC = Diethylaluminiumchloride
 DEDTC-Co = Cobalt diethyl dithiocarbamate
 DEDTPH-Co = Cobalt diethyl dithiocarbamate
 DEDTPH-Co = Cobalt diethyl dithiophosphate
 DiPDTPH-Co = Cobalt *O,O'*-di-isopropyl dithiophosphate
 DTC = Dithiocarbamate
 DTD = Dithioderivative
 DTPH = Dithiophosphate
 EASC = Ethylaluminiumsesquichloride
 Et = Ethyl
 GPC = Gel permeation chromatography
 iPr = iso-Propyl
 IR = Infra-red
 M = Monomer (butadiene-1,3)
 Me = Transition metal
 MM = Molecular mass
 NGDTPH-Co = Cobalt *O,O'*-di-(2,2'-methylene-bis-4-methyl-6-*tert*.butylphenyl) dithiophosphate
 Ni = Nickel
 PBD = Polybutadiene
 TAA = Trialkylaluminium
 TEA = Triethylaluminium
 X-Co = Cobalt *O,O'*-di-(3,5-di-*tert*.butyl-4-hydroxyphenyl) dithiophosphate
 Xh = Canthogenate

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