Gas Phase Polymerization of Butadiene on Heterogenized Cobalt-containing Catalytic Dithiosystems

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Received 23 June 2008; accepted 25 May 2009

ABSTRACT

The gas phase polymerization of butadiene on new heterogenized bifunctional cobalt-containing catalytic dithiosystems was studied. Earlier, some highly active and efficient homogeneous bifunctional catalyst-stabilizers were developed on the bases of Ni- and Co-dithioderivatives (such as O,O-disubstituted dithiophosphates and N,N-dithiocarbamates) in combination with aluminium organics (such as dialkylaluminiumchlorides, alkylaluminium-dichlorides, and aluminoxanes) for butadiene solution polymerization and simultaneous stabilization of end polymer. The problem of separating homogeneous catalysts from the reaction medium is still the most important obstacle in blocking its large scale applications in industry. A number of potential methods for homogeneous catalyst separation and recovery have been or are presently being developed, such as a two-phase catalysis and heterogenization on inorganic or organic supports. Cobalt-containing bifunctional catalytic dithiosystems have been heterogenized on various supports (such as silica gels, aluminium oxides, zeolites, carbon black, etc.) by direct deposition or pre-alumination methods. The obtained data demonstrate that the pre-alumination method of immobilization of bifunctional cobalt-containing catalytic dithiosystems shows very high activity in gas phase polymerization of butadiene. These catalysts’ productivity reaches ~650.0-2200.0 kg PBD/g Co.h, which is much higher than the output of solution process using the same homogeneous catalysts (57.0 kg PBD/g Co.h) and the known gas phase process using the heterogenized neodymium-catalysts (500.0 kg PBD/g Nd.h). High activities of heterogenized bifunctional cobalt-containing catalytic dithiosystems allow the development of principally a new ecologically favourable and economically feasible technology of butadiene gas phase polymerization process by involving them as raw materials not only for pure butadiene, but also butadiene as C4 fraction of pyrolysis product.

INTRODUCTION

The technological methods used for the production of polydienes, especially, polybutadiene (PBD) have not changed for more than 50 years. Its polymerization has been carried out by solution method, using homogeneous Ti, Co, and Ni-containing Ziegler-Natta type catalytic systems. The problem of separating homogeneous catalysts from the reaction medium is still the most important obstacle which makes large scale industrial applications unfeasible. Another major drawback of polymerizations in organic solvents is the inefficient...
removal and recovery of the solvents and monomers after polymerization stage which often requires more processing steps and energy consumption than the actual polymerization.

Gas phase polymerization methods for the production of thermoplastics such as polyethylene and polypropylene have proved to be particularly advantageous and have gained acceptance. The gas phase process has many advantages over the solution processes. Solvents are not used in this process, therefore there are no technological, economic, and ecological problems concerning cleaning and drying the solvents, washing off catalyst residues from the polymerizate, polymer degassing, polymer solubility, and viscosity of reaction medium. In gas phase polymerization process, also the complicated procedures of aggregation and separation of polymer from solution, as needed in solution polymerization, are excluded. This leads to cutting down the cost of construction and operation and also reducing environmental pollution.

The solvent-free polymerization of dienes from the gaseous phase represents a new procedure which has not yet been realized on industrial scale, which offers and at present it does not yet technically meet substantial ecological, economic, energetic, and safety-relevant advantages.

Study on gas phase polymerization of butadiene with neodymium Ziegler-catalysts in laboratory scale was first carried out by Berlin Technical University in 1993 [1-6]. The productivity of these heterogenized neodymium catalyst systems was very low ~500.0 kg PBD/g Nd.h. Many polymer manufacturers also have reported gas phase processes for diene monomers, and several have established significant patent portfolios including Bayer, Bridgestone, and Union Carbide [7-15]. To date, Bayer appears to be closest to commercializing a gas phase process for producing polybutadiene rubber [7-12].

However, the exciting catalytic systems offered for gas phase polymerization of butadiene (lanthanides, cobalt or nickel-containing) are characterized by essential shortcomings related to their low catalytic activity and ability to accelerate the oxidative ageing and degradation of PBD [1-13].

Earlier we have developed the highly active and efficient homogeneous bifunctional catalyst-stabilizers on the bases of Ni- and Co-dithioderivatives (such as \(O,O\)-disubstituted dithiophosphates, \(N,N\)-dithiocarbamates, xanthogenates) in combination with aluminium organic compounds (such as dialkylaluminium chlorides, alkylaluminium dichlorides, aluminoxanes) for butadiene polymerization and simultaneous stabilization of the polymer end product [14-18]. These catalysts have shown high activity and stereoselectivity in homogeneous polymerization of butadiene. Their productivity has reached 5.0-109.0 kg PBD/g Me.h with intrinsic viscosity in the range of 0.08-3.5 dL/g, and 1.4-cis content of 80.0-96.0%. After polymerization such catalysts are not washed out and remain in the polymer which effectively stabilizes the system without additional involvement of antioxidants against thermo- and photo-oxidative ageing in storage.

Heterogenization of these new bifunctional cobalt-containing catalytic dithiosystems allows a process of very high productivity, 650.0-2200.0 kg PBD/g Co.h, which is much higher than the output of solution process using the same homogeneous catalysts (5.0-109.0 kg PBD/g Co.h) and the known gas phase process using the heterogenized neodymium-catalysts (500.0 kg PBD/g Nd.h).

In this article, the results of gas phase polymerization of butadiene obtained in the presence of new heterogenized bifunctional cobalt-containing catalytic dithiosystems which have been developed by us are presented for the first time.

**EXPERIMENTAL**

**Materials**

In preparation of homogenization catalytic complex for heterogenization process toluene was used as a solvent. After predrying over metallic sodium for 24 h, toluene was distilled over metallic Na 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 of 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 by molecular sieves. Traces of inhibitor were removed with soda asbestos.

Diethylaluminiumchloride (Et₂AlCl-DEAC) and triethylaluminium (TEA) obtained from Redkino plant (Moscow, Russian Federation) with a minimum purity of 85.0% (wt), were used as received. The DEAC (or TEA), diluted to 10% (vol) in dry toluene for polymerizations, was drawn from a crown-sealed beverage bottle kept in a glove box. Methylaluminoxane (MAO) was obtained from Aldrich and used without purification. Aluminoxanes have cyclic, linear-double, and linear structures. But, oligomeric aluminoxanes are usually presented as linear-chain structure by a general formula of [−O-Al(R)−]ₙ. The characteristic structure of aluminoxanes component is the Al-O-Al linkage. According to literature [19] the molecular weight of MAO is 948.

Organic dithioderivatives (dithiophosphates and dithiocarbamates) of cobalt have been synthesized according to literature [14]. Some characteristic features of the synthesized dithioderivatives are shown in Table 1.

**Methods of Heterogenization of Bifunctional Cobalt-containing Catalytic Dithiosystems on Supports**

Where necessary, manipulations were carried out under dry, oxygen-free argon or nitrogen in Schlenk-type apparatus with appropriate techniques and gas tight syringes. For preparing the homogeneous metallocomplex catalyst the desired volume of toluene, monomer, DEAC (or TEA), and cobalt components solutions were added to the reactor (100 mL volume) with magnetic stirring at oxygen-free atmospheric pressure and temperature control. The usual order of adding catalyst components in preparing homogeneous metallocomplex catalyst was: solvent, cobalt component, aluminium organic compound (at -78°C) and finally monomer.

**Supports**

Many types of solid materials have been investigated as support materials for the immobilization of metallocomplex catalysts: inorganic materials (SiO₂, MgCl₂, Al₂O₃, zeolite, etc.) and polymeric materials (polystyrene, polysiloxane, etc.). The most common support used is silica gel, due to its low cost and ease of functionalization. The silica gel surface contains hydroxyl and siloxane functional groups, which are useful in surface modification and catalyst immobilization.

**Typical Immobilization Methods**

There are many ways that metallocomplex catalysts have been immobilized on supports [20, 21] and we have used the three main techniques for metallocomplex catalysts immobilization.

The first approach called the “direct deposition” (also called grafting or impregnation) and is to physisorb a complex such as a coordination metal compound onto the support’s surface [20, 21]. This is the most convenient method of metallocomplex catalysts immobilization. In a typical process, some pretreated (calcined and partially thermally dehydroxylated) silica gel is stirred with a solution of a cobalt compound of metallocomplex catalyst in inert atmosphere at room temperature or elevated temperatures for a period of time. Then, the slurry is filtered, and the remaining solid product is washed with solvent several times to remove weakly adsorbed metallocomplex compound molecules. The washed product is dried under vacuum to remove the solvent. The metallocomplex compound is believed to react with hydroxyl groups on silica gel surface and bond to the surface through an M-O-Si bond.

We have supported cobalt-containing organic dithioderivatives on silica gel dehydrated at 120-200°C under vacuum. Many parameters need to be considered in the direct deposition method, such as metal loading, silica gel activation temperature, grafting temperature and time, solvent, etc. Supported metallocomplex catalysts prepared using the direct deposition method usually exhibit low activities for butadiene polymerization. As it is reported [20, 21], low activity is attributed to: the steric demand of the surface, which prevents monomers from accessing the active sites; the donating/poisoning effect of the oxygen atom in the M-O-Si linkage; the bimolecular deactivation of two adjacent surface metal centres when the surface metallocomplex compound loading is high.

A second method is the “pre-alumination” immobilization method. This is the process in which
<table>
<thead>
<tr>
<th>Symbol of DTC-Co</th>
<th>Chemical formula</th>
<th>Nomenclature</th>
<th>Yield, % by mass</th>
<th>Melting point (ºC)</th>
<th>Molecular mass, found/calculated</th>
<th>Elemental composition, found/calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCDTPh-Co</td>
<td><img src="image" alt="CDCDTPh-Co" /></td>
<td>Cobalt O,O-di-4-methyl-phenyl dithiophosphate</td>
<td>75</td>
<td>107</td>
<td>676.0/677.0</td>
<td>49.33/49.64 4.21/4.14 8.85/9.16 18.75/18.91</td>
</tr>
<tr>
<td>DTBPhDTPh-Co</td>
<td><img src="image" alt="DTBPhDTPh-Co" /></td>
<td>Cobalt O,O-di-4-t-butylphenyl dithiophosphate</td>
<td>82</td>
<td>192</td>
<td>841.0/844.9</td>
<td>56.6/56.81 5.9/6.1 7.18/7.34 15.4/15.2</td>
</tr>
<tr>
<td>DPhDTPh-Co</td>
<td><img src="image" alt="DPhDTPh-Co" /></td>
<td>Cobalt O,O-diphenyl dithiophosphate</td>
<td>85</td>
<td>136</td>
<td>618.0/620.9</td>
<td>46.1/46.3 3.3/3.2 9.87/9.98 20.5/20.6</td>
</tr>
<tr>
<td>TBPh-Co</td>
<td><img src="image" alt="TBPh-Co" /></td>
<td>Cobalt 2,2'-thio-bis-O,O-di-4-t-butylphenyl dithiophosphate</td>
<td>80</td>
<td>276</td>
<td>905.1/905.0</td>
<td>53.2/53.0 5.2/5.3 6.71/6.85 21.5/21.2</td>
</tr>
<tr>
<td>4-m,6-TBPh-Co</td>
<td><img src="image" alt="4-m,6-TBPh-Co" /></td>
<td>Cobalt 2,2'-thio-bis-O,O-di-4-methyl-6-t-butylphenyl dithiophosphate</td>
<td>61</td>
<td>200</td>
<td>960.0/961.0</td>
<td>54.8/54.9 6.1/5.8 6.21/6.46 19.4/19.8</td>
</tr>
<tr>
<td>X-Co</td>
<td><img src="image" alt="X-Co" /></td>
<td>Cobalt O,O-di-(3,5-di-t-butyl-4-hydroxyphenyl) dithiophosphate</td>
<td>85</td>
<td>210</td>
<td>1135/1132</td>
<td>59.8/59.3 7.5/7.4 5.60/5.47 11.4/11.3</td>
</tr>
<tr>
<td>NGDTPh-Co</td>
<td><img src="image" alt="NGDTPh-Co" /></td>
<td>Cobalt O,O-di-(2,2'-methylene-bis-4-methyl-6-t-butylphenyl) dithiophosphate</td>
<td>87</td>
<td>195</td>
<td>856.2/857.0</td>
<td>55.9/56.4 6.8/7.0 7.16/7.2 14.8/14.9</td>
</tr>
<tr>
<td>DEDTC-Co</td>
<td><img src="image" alt="DEDTC-Co" /></td>
<td>Cobalt N,N-diethyl dithiocarbamate</td>
<td>95</td>
<td>$T_{\text{decomp.}}$</td>
<td>355.0/356.0</td>
<td>33.8/33.91 5.6/5.8  - 36.1/36.2</td>
</tr>
</tbody>
</table>

Table 1. Physico-chemical and analytical data of used cobalt dithiocompounds.
the support material is in contact with a cocatalyst (either methylaluminoxane or an alkylaluminium halogenids) before impregnating with a metallocomplex compound [20,21]. In one process, silica gel is stirred with a solution of cocatalyst (MAO) and then filtered (Scheme I). The solid portion is washed and dried in vacuum to obtain the MAO-modified silica gel. A minor modification of this process is to add n-decane to the slurry of silica gel and MAO in toluene to precipitate the MAO onto the silica gel. In another process, supported MAO is generated in situ by reacting TMA with water in the presence of silica gel, or by reacting TMA with water adsorbed on the surface of silica gel without dehydration (Scheme II). The subsequent metallocomplex catalyst cobalt compound impregnation process is similar to that of the direct deposition method [20,21].

When silica is treated with MAO, the surface hydroxyl groups react with MAO and release CH$_4$ (Schemes I and II), as MAO is bonded to silica gel through Si-O-Al bonds. The metallocomplex compound molecules are thus immobilized on silica gel by ionic interaction with the bonded MAO and become active catalytic species at the same time. The ionic interaction is weak, so the active species may be able to migrate over the MAO covered silica gel surface, resulting in a similar environment of the active species as that in homogeneous solution [20,21]. Therefore, the polymers produced by these supported catalysts have similar properties as those produced by corresponding homogeneous metallocomplex catalysts.

We also used a third method consisting of the covalent tethering method to immobilize a homogeneous metallocomplex catalyst on silica gel that is close to the pre-alumination method. In this method the homogeneous metallocomplex catalyst is prepared by the reaction of a solution of cobalt compound of metallocomplex and MAO (or an alkyl aluminium halogenides) in the presence of monomer molecules, and then pre-aluminated silica gel is added to the solution [20,21] (Scheme III).

The slurry is stirred and dried to form the supported catalyst. Since the cobalt compound of metallocomplex catalyst has been activated in solution by MAO in the presence of monomer molecules, the immobilization should occur between excess MAO and silica gel surface. The structure of the supported catalyst prepared using this method should resemble that of the supported catalyst using the prealumination method [20,21].

The methods of heterogenization of homogeneous bifunctional catalyst-stabilizers and calculated concentration of cobalt in support of heterogenized catalytic dithiosystems are shown in Table 2.

**Polymerization Procedure**

In a typical experiment, the polymerization reaction
was evacuated whilst hot, allowed to cool and then filled with dry, oxygen-free argon or nitrogen. Heterogenized catalyst and butadiene are continuously transferred from the calibrated reservoirs to the polymerization reactor. Continuous experiments on gas phase polymerization of butadiene were carried out in a 500-mL double-walled glass reactor with constant supply of gaseous butadiene at atmospheric pressure.

All polymerizations were conducted at 25ºC. After polymerization the polymerizate was poured into ethanol (methanol) and the reaction was terminated. The precipitated polymer was (if necessary) washed several times with ethanol (methanol). The polybutadiene was dried at 40ºC in a vacuum to constant weight and stored under argon or nitrogen.

**Molecular Mass and Structure Determinations**

The viscosity of dilute solutions of 1,4-cis and 1,4-cis + 1,2-polybutadienes was measured with a Ubbelohde viscometer in toluene at 30ºC at the concentration of 0.2 g/dL. The intrinsic viscosity \([\eta]\) was estimated by double extrapolation \(\eta_{sp}/C\) and \(\ln \eta_{rel}/C\) to \(C \rightarrow 0\) where, \(\eta_{sp}\) is the specific viscosity, \(C\) is the solution concentration (g/dL), and \(\eta_{rel}\) is the relative viscosity [22].

The molecular mass of high molecular 1,4-cis polybutadiene and 1,4-cis + 1,2-polybutadiene, respectively, was determined by viscosimetry method [22] using the following relationships:

\[
[\eta]_{30(\text{toluene})} = 3.05 \times 10^{-4} \times M^{0.725}
\]

\[
[\eta]_{30(\text{toluene})} = 15.6 \times 10^{-5} \times M^{0.75}
\]

The molecular mass (\(\bar{M}_w\) and \(\bar{M}_n\)) and molecular mass distribution (\(\bar{M}_w/\bar{M}_n\)) of polybutadienes were measured by a gel permeation chromatograph (GPC), constructed in Czech Republic with a 6000A pump, original injector, R-400 differential refractive index detector, styrargel columns with nominal exclusion of 500, \(10^3\), \(10^4\), \(10^5\), and \(10^6\). The GPC operated at a flow rate of 0.8 mL/min with \(o\)-dichlorobenzene as
Table 2. Heterogenization methods of cobalt-containing catalytic dithio systems.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Method of heterogenization</th>
<th>Support preparation</th>
<th>Heterogenization conditions</th>
<th>Concentration of cobalt on support (calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAT.1</td>
<td>Direct deposition</td>
<td>Silica gel dehydrated at 150ºC during 3 h.</td>
<td>The toluene solution of X-Co is physisorb onto the support during 60 min. The slurry is filtered; the remaining solid product is washed some times with toluene and dried under vacuum and inert atmosphere.</td>
<td>[Co] = 1.0×10⁻⁷ mol/g; AI:Co = 100:1; ([DCDTPh-Co] = 6.77×10⁻⁵ g/g or [Co] = 5.9×10⁻⁶ g/g; Co = 0.00059%</td>
</tr>
<tr>
<td>CAT.2</td>
<td>Direct deposition</td>
<td>Silica gel dehydrated at 150ºC during 3 h and then at 450ºC during 2 h.</td>
<td>The toluene solution of X-Co+DEAC is physisorb onto the support during 60 min. The slurry is filtered; the remaining solid product is washed some times with toluene and dried under vacuum and inert atmosphere.</td>
<td>[Co] = 1.0×10⁻³ mol/g; AI:Co = 1000:1; ([DCDTPh-Co] = 6.77×10⁻⁵ g/g or [Co] = 5.9×10⁻⁷ g/g; Co = 0.000059%</td>
</tr>
<tr>
<td>CAT.3</td>
<td>Direct deposition</td>
<td>Silica gel dehydrated at 650ºC during 5 h.</td>
<td>The toluene solution of X-Co+MAO is physisorb onto the support during 60 min. The slurry is filtered; the remaining solid product is washed some times with toluene and dried under vacuum and inert atmosphere.</td>
<td>[Co] = 1.0×10⁻⁷ mol/g; AI:Co = 100:1; ([DCDTPh-Co] = 6.77×10⁻⁵ g/g or [Co] = 5.9×10⁻⁷ g/g; Co = 0.000059%</td>
</tr>
<tr>
<td>CAT.4</td>
<td>Pre-alumination</td>
<td>Silica gel dehydrated at 200ºC during 6 h and at 25ºC the toluene solution of DEAC ([Al] = 4 mmol/g support) was added, the slurry is filtered, the remaining solid product is washed some times with toluene and dried under vacuum and inert atmosphere.</td>
<td>The toluene solution of X-Co+DEAC+butadiene complex is physisorb onto the support during 60 min. The slurry is filtered; the remaining solid product is washed some times with toluene and dried under vacuum and inert atmosphere.</td>
<td>[Co] = 1.0×10⁻⁷ mol/g support; AI:Co = 100:1; ([DCDTPh-Co] = 6.77×10⁻⁵ g/g support or [Co] = 5.9×10⁻⁶ g/g support; Co = 0.000059%</td>
</tr>
<tr>
<td>CAT.5</td>
<td>Pre-alumination</td>
<td>Silica gel dehydrated at 200ºC during 2 h and at 25ºC was added the toluene solution of MAO ([Al] = 4 mmol/g support), the slurry is filtered, the remaining solid product is washed some times with toluene and dried under vacuum and inert atmosphere.</td>
<td>The toluene solution of X-Co+DEAC+butadiene complex is physisorb onto the support during 60 min. The slurry is filtered; the remaining solid product is washed some times with toluene and dried under vacuum and inert atmosphere.</td>
<td>[Co] = 1.0×10⁻⁷ mol/g support; AI:Co = 100:1; ([DCDTPh-Co] = 6.77×10⁻⁵ g/g support or [Co] = 5.9×10⁻⁶ g/g support; Co = 0.000059%</td>
</tr>
</tbody>
</table>
solvent. The sample concentration was kept at about 0.3-0.6% with a sample volume of 100-200 mL. GPC instrument was calibrated according to the universal calibration method by using narrow molecular weight polystyrene standards [23].

The microstructure of the polybutadiene was determined by a Beckman IR spectrophotometer [36,37]. Typical IR spectrum of 1,4-cis-polybutadiene is given in Figure 1. As it is shown in Figure 1, 1,4-cis-, 1,4-trans-, and 1,2-polybutadienes are different in the observed peaks between 600 cm\(^{-1}\) and 1100 cm\(^{-1}\) in wavenumbers (wavelength between 9 and 16 micrometers), however location of units has been shifted: cis, 740 cm\(^{-1}\); 1,2, 912 cm\(^{-1}\); and 1,4-trans, 960-970 cm\(^{-1}\).

**RESULTS AND DISCUSSION**

**Influence of Experimental Conditions on the Main Parameters of Gas Phase Polymerization of Butadiene**

The catalytic activity of some samples of hetero-
nized bifunctional cobalt-containing catalytic dithiosystems in gas phase polymerization of butadiene was investigated and the results are summarized in Table 3 in comparison with the known homogeneous bifunctional cobalt-containing catalytic dithiosystems and gas phase process of Berlin Technical University using the heterogenized neodymium-catalysts.

The data demonstrate that the pre-alumination method of immobilization of bifunctional cobalt containing catalytic dithiosystem with X-Co shows a very high activity in gas phase polymerization of butadiene. Results of Table 3 show that at reaction conditions: [Co] = 1.0×10⁻⁷ mol/g support; T = 25°C catalysts productivity reaches ~1700.0 kg PBD/g Co.h, which is much higher than the output of solution process using the same homogeneous catalyst X-Co+DEAC (57.0 kg PBD/g Co.h) and gas phase process of Berlin Technical University using the heterogenized neodymium-catalysts (500.0 kg PBD/g Nd.h).

High catalytic activities are shown by methods of heterogenization in CAT.4 and CAT.5. Therefore, the investigations of activity and stereoselectivity of cobalt catalysts with various organic dithioderivatives were investigated using these heterogenization methods.

Research results are shown in Table 4. As it is observed in Table 4, by changing the ligands in cobalt compounds it is possible to change the catalyst productivity and stereoregularity widely. The most catalytic activity and stereoselectivity were obtained using X-Co, DCDTPh-Co, and NGDTPh-Co as components of heterogenized catalyst. Their productivity reached 1340.0-1700.0 kg PBD/g Co.h, intrinsic viscosity in the range of 2.5-3.8 dL/g, and the 1.4-cis content obtained was 91.0-96.0%.

Heterogenized DEDTC-Co+DEAC catalytic system allows the production of high molecular 1,4-cis + 1,2-PBD with 1,4-cis content of 62.0%, 1,2-content of 35.0%, 1,4-trans content of 3.0%, intrinsic-viscosity of 1.94 dL/g with the productivity 850.0 kg PBD/g Co.h.

High activities of heterogenized bifunctional cobalt-containing catalytic dithiosystems allowed us to develop principally a new ecologically favourable and economically feasible technology of butadiene gas phase polymerization process by not only involving pure butadiene as a raw material, but also butadiene in crude C₄ stream [26].

As it is seen from experimental data of Table 5, in polymerization of butadiene in crude C₄ stream these heterogenized cobalt-containing catalytic dithiosystems, catalytic activity and stereoselectivity are decreased relative to polymerization of pure butadiene, but more than in homogeneous processes. Their productivity reaches 650.0-1200.0 kg PBD/g Co.h, intrinsic viscosity in the range of 2.1-2.8 dL/g, and the 1.4-cis content of 90.0-93.0%.

In polymerization of butadiene in crude C₄ stream in the presence of heterogenized DEDTC-Co+DEAC catalytic system a product of 1.4-cis + 1.2-PBD with

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction time (min)</th>
<th>Productivity (kg PBD/g Co.h)</th>
<th>Intrinsic viscosity [η] (dL/g)</th>
<th>Molecular mass</th>
<th>Microstructure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M₆ × 10⁻³</td>
<td>Mₙ/M₆</td>
</tr>
<tr>
<td>CAT.1</td>
<td>60</td>
<td>340</td>
<td>3.4</td>
<td>330</td>
<td>2.75</td>
</tr>
<tr>
<td>CAT.2</td>
<td>45</td>
<td>510</td>
<td>3.8</td>
<td>466</td>
<td>2.6</td>
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<tr>
<td>CAT.3</td>
<td>90</td>
<td>1250</td>
<td>4.85</td>
<td>950</td>
<td>2.2</td>
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<td>CAT.4</td>
<td>60</td>
<td>1450</td>
<td>3.3</td>
<td>310</td>
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<td>CAT.5</td>
<td>45</td>
<td>1700</td>
<td>3.8</td>
<td>466</td>
<td>2.6</td>
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<tr>
<td>CAT.6</td>
<td>90</td>
<td>950</td>
<td>4.1</td>
<td>500</td>
<td>2.5</td>
</tr>
<tr>
<td>CAT.7* (BTU)</td>
<td>60</td>
<td>500</td>
<td>5.2</td>
<td>1500</td>
<td>2.3</td>
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<tr>
<td>CAT.8**</td>
<td>15</td>
<td>57</td>
<td>3.5</td>
<td>450</td>
<td>2.5</td>
</tr>
</tbody>
</table>

(*) (**) as in Table 2 footnotes.
catalyst productivity of 350.0 kg PBD/g Co.h and 1,4-cis content of 65.0%, 1,2-content of 30.0%, and 1,4-trans content of 5.0%, with intrinsic viscosity of 2.1 dL/g was obtained.

The behaviour of changing ligands in cobalt compound is similar to those of homogeneous catalyst for polymerization of butadiene [16]. High activities of X-Co, DCDTPh-Co, and NGDTPh-Co in butadiene polymerization have been explained by high solubility of these compounds in toluene solvent and forming stable metallocomplex catalytic active centres with high concentration. These expected nano-sized active centres, covalently tethered on support, allowed very high productivity comparing to solvent polymerization.

Heterogenized catalyst particles were introduced into the reactor by an inert gas flow or gaseous monomer. The particles are kept in the reaction zone of the reactor by a strong gaseous butadiene (or crude C4 steam) flow. The particles flow and separate from each other in the reaction zone, so it is called a “fluidized bed”. Under the polymerization conditions (a temperature below 80°C and a pressure below 2 MPa), butadiene polymerizes on the particles, and gradually the particles grow into tiny polymer corpuscles. Polymer particles above certain size cannot keep flowing in the reaction zone, so they fall to the bottom of the reactor, where they are removed as product. The polymer particles removed from the reactor can be directly packed as final product.

Gaseous butadiene has three processing functions: the monomer for the polymerization, the medium to remove heat generated in the polymerization, and the gas flow to keep particles flow and being separated. One major difficulty for research laboratories is the enormous difficulty and cost of design and construction even in a small-scale version of a reactor in order to study gas phase polymerization process.

In the supported Ziegler-Natta catalysts, the precursor species are dispersed on the surface of the support particles, so theoretically, they can all be activated and increase activity.

As it was shown earlier the direct deposition method is simple and convenient, but the supported catalysts prepared using this method usually have low polymerization activities due to the influences of the silica surface, e.g., steric hindrance and poisoning effect (Table 3).

In the supported homogeneous catalysts prepared using the pre-alumination method, active sites have appreciable freedom of movement on the support, so the catalytic properties of the supported active sites resemble those of the homogeneous analogs and the polymers obtained are similar to those produced by the homogeneous analogs (Table 3). However, the nature of the weak ionic interactions that bind the active sites to the MAO-covered support is not clear and is difficult to study.

<table>
<thead>
<tr>
<th>Cobalt dithiocompound (DTC-Co)</th>
<th>Method of heterogenization</th>
<th>Reaction time (min)</th>
<th>Productivity (kg PBD/g Co.h)</th>
<th>Intrinsic viscosity [η] (dL/g)</th>
<th>Molecular mass (M_w \times 10^{-3})</th>
<th>Microstructure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCDTPh-Co</td>
<td>CAT.4</td>
<td>60</td>
<td>1340</td>
<td>2.5</td>
<td>250</td>
<td>93 5 2</td>
</tr>
<tr>
<td>DCDTPh-Co</td>
<td>CAT.5</td>
<td>60</td>
<td>1650</td>
<td>2.6</td>
<td>270</td>
<td>95 4 1</td>
</tr>
<tr>
<td>DTBPh-DTPh-Co</td>
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<td>60</td>
<td>750</td>
<td>3.1</td>
<td>320</td>
<td>93 5 2</td>
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<td>93 5 2</td>
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<td>CAT.5</td>
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<td>NGDTPh-Co</td>
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<td>NGDTPh-Co</td>
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<td>3.3</td>
<td>350</td>
<td>62 35 3</td>
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<tr>
<td>DEDTC-Co</td>
<td>CAT.4</td>
<td>60</td>
<td>1450</td>
<td>3.3</td>
<td>310</td>
<td>91 6 3</td>
</tr>
</tbody>
</table>

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The covalent tethering method avoids the disadvantage of the direct deposition method by putting a covalent spacer between an active site and the support surface. The interface between an active site and the support is a covalent tether, which is somewhat easier to characterize. The flexibility of a long single-tether also provides the active site a pseudo-solution environment. However, the flexibility of the long single-tether also provides a route for direct interaction of the active site with the surface, so the active site is in a similar situation as that of an active site in a supported catalyst prepared using the direct deposition method. The covalent tethering method should not only immobilize a homogeneous catalyst firmly, but it also preserves the most useful features of the catalyst, e.g., high activity and stereoselectivity, as well as lifetime (Tables 4 and 5).

An important aspect of the immobilized homogeneous catalysts is the stability of the active species on the supports. Unstable active species of the immobilized catalysts may leave or migrate on the support during polymerization, causing many problems. In the slurry polymerization process, if unstable active species leave the support and become free in the solution, they just act as homogeneous catalyst and polymerize monomers. The polymer produced by the freed active species in solution causes poor morphology of the polymer product and reactor fouling. Reactor fouling means that the polymer produced by the freed active species will adhere to the surface of the mechanical stirrer or the internal surface of the reactor and form a polymer layer, so the efficiency of the stirrer and the heat-transfer efficiency of the reactor are greatly reduced. In the gas phase polymerization process, the migration of unstable active species from interior of the catalyst particles to the surface will result in polymer product of poor molecular weight distribution and micro-structural dispersion, etc. Both poor morphology and reactor fouling are manifestations of “catalyst leaching”. Catalyst leaching has been found in the first and second methods of immobilization of catalysts. No leaching of active species from the support was observed in the covalent tethering method.

**CONCLUSION**

A new highly active and stereoselective heterogeneous bifunctional cobalt-containing catalytic dithiosystems for butadiene gas phase polymerization has been developed. Based on organic dithiocompounds of cobalt (O,O-dithiophosphates and N,N-dithiocarbamates) in combination with aluminum organic compounds (DEAC, TEA, and MAO) and heterogenized by the methods of pre-alumination and covalent tethering on silica gel support these catalysts provide the preparation of high molecular mass 1.4-cis (91.0-96.0%) or 1.4-cis + 1.2 (1.4-cis of 62.5 and 1.2 of 35.0%) polybutadienes with productivity of 650.0-2200.0 kg PBD/g Co.h and intrinsic viscosity of 2.5-3.8 dL/g.

### Table 5. Catalytic activities of heterogenized DTC-Co + AOC catalyst systems in gas phase polymerization of butadiene in crude C₄ stream composition of a crude C₄ stream, wt%: C₃ hydrocarbons -0.3; butanes-3.4-6.5; 1-butene-13.7-16.0; cis-2-butene-4.8-5.3; trans-2-butene-5.5-6.6; isobutene-22.2-27.4; 1,3-butadiene-37.0-47.5; C₅ hydrocarbons-0.5; reaction conditions: [Co] = 1.0×10⁻⁷ mol/g support; T = 25°C.

<table>
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<tr>
<th>Cobalt dithiocompound (DTC-Co)</th>
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<th>Molecular mass</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mₜ × 10⁻³</td>
<td>Mₜ/Mₚ</td>
</tr>
<tr>
<td>DCDTPh-Co</td>
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<td>120</td>
<td>650</td>
<td>2.3</td>
<td>250</td>
<td>1.56</td>
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<td>235</td>
<td>1.74</td>
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<tr>
<td>X-Co</td>
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<td>120</td>
<td>750</td>
<td>2.8</td>
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<td>X-Co</td>
<td>CAT.5</td>
<td>90</td>
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<td>1.54</td>
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<td>NGDTPh-Co</td>
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<td>NGDTPh-Co</td>
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<td>350</td>
<td>2.1</td>
<td>220</td>
<td>2.10</td>
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</table>

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High activities of these catalysts allow the development of a new ecologically favourable and economically benefiting technology of butadiene gas phase polymerization process by involving as a raw material not only pure butadiene, but also butadiene in crude C₄ stream.

ACKNOWLEDGEMENTS

Financial support of this work by the Institute of Petrochemical Processes Azerbaijan National Academy of Sciences, Baku, Azerbaijan Republic, is gratefully acknowledged.

SYMBOLS AND ABBREVIATIONS

AOC            : aluminium organic compound  
DCDTPh-Co : cobalt $O,O'$-di-4-methylphenyl dithiophosphate  
DEAC            : diethylaluminiumchloride  
DEDTC-Co : cobalt diethyl dithiocarbamate  
DEDTPh-Co : cobalt diethyl dithiophosphate  
DTC : dithiocompound  
DTPh : dithiophosphate  
GPC : gel permeation chromatography  
IR : infra-red  
MAO : methylaluminoxane  
NGDTPh-Co : cobalt $O,O'$-di-(2,2'-methylene-bis-4-methyl-6-tert.butylphenyl) dithiophosphate  
PBD : polybutadiene  
TEA : triethylaluminium  
4-m,6-TBPh-Co: cobalt 2,2'-thio-bis-$O,O$-di-4-methyl-6-tert.butylphenyl dithiophosphate  
X-Co : cobalt $O,O'$-di-(3,5-di-tert.butyl-4-hydroxyphenyl) dithiophosphate

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