



# **Copolymerization of Butadiene with Ethylene in the Presence of Ni-containing Organometallic Catalytic Systems and Different Modifiers**

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## **Authors' contributions**

*This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.*

## **Article Information**

DOI: 10.9734/AJOPACS/2021/v9i330136

### Editor(s):

(1) Dr. Thomas F. George, University of Missouri- St. Louis, USA.

### Reviewers:

(1) Rasha S. Kamal, Egyptian Petroleum Research Institute, Egypt.

(2) Nzuetom Mbami Steve Wilfried, China University of Petroleum, China.

(3) Mahmoud Bekhit Mohamed Abbass, Egyptian Petroleum Research Institute, Egypt.

Complete Peer review History: <https://www.sdiarticle4.com/review-history/73734>

**Original Research Article**

**Received 07 July 2021**  
**Accepted 17 September 2021**  
**Published 27 September 2021**

## **ABSTRACT**

Copolymerization of ethylene with butadiene was carried out in the presence of nickel diethyldithiocarbamate and various modifiers. Triphenylphosphines were selected as modifiers. Solutions of nickel diethyldithiocarbamates and triphenylphosphines in aromatic solvents of various concentrations have been prepared. Their physicochemical parameters, particle sizes in solutions, as well as mutual solubility were determined. It was demonstrated that these complexes are readily soluble in aromatic solvents, and the particle size in solution is in the nanometer range. These complexes were tested in the processes of copolymerization of ethylene with butadiene in combination with various cocatalysts (tri-, diethylaluminum chloride). The products synthesized in their presence were analyzed by various physicochemical methods and their structure was confirmed. It has been shown that oligomeric and copolymer products with the required structure can be in fact synthesized in the presence of these catalytic systems. The activity and selectivity of catalytic systems have been comparatively tested in liquid phase copolymerization processes. The composition and conditions have been found to have a significant effect on the activity and structure of the resulting products.

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**Keywords:** *Ethylene and butadiene copolymerization; ethylene polymerization; (non)metallocene catalysts; nickel-containing complexes; modifiers.*

## 1. INTRODUCTION

Ethylene, propylene, butylene, butadiene (divinyl), being highly reactive compounds, play an important role in the organic synthesis industry. Of the numerous reactions in which olefins thrive, the processes of polymerization, chlorination, oxidation, hydration, oxosynthesis and some others are of the greatest practical importance [1,2].

Anionic coordination polymerization of these monomers is a process that occurs under the influence of Ziegler-Natta catalysts, which are complexes of transition metal halides with organometallic compounds. Typical catalysts of this type are titanium tetrachloride - triethylaluminum and vanadium tetrachloride - diethylaluminum chloride; other systems are also known. Evidently, other catalysts act similarly, for example, dicobaltoctacarbonyl and some  $\eta^5$ -allylnickel halides. The exact nature of the reactive intermediates formed by these systems continues to be a subject for debate, but polymerization is likely to proceed through the insertion of the vinyl monomer into the transition metal-carbon bond. The most important monomers entering into the reaction of coordination polymerization are ethylene, propylene, butadiene-1,3 and isoprene.

Ethylene, which has only one relatively accessible electron pair, namely the p-electrons of the double bond, can participate in the formation of complexes of this type, but dienes, such as butadiene or isoprene, can occupy two free levels with two electron pairs of both conjugated double bonds. Since the p-electron beds of these compounds are not as accessible, as the lone electron pairs in oxygen or nitrogen atoms, the resulting complexes are less stable and more difficult to isolate and characterize in pure form. It is possible that it is precisely the low stability of such complexes that makes them highly reactive transition states for a polymerization reaction. Polymers with side groups can also be obtained by copolymerization of linear, non-polar monomers such as ethylene, butadiene, etc. Formation of a linear chain that does not contain side groups depends on the reaction conditions (temperature, catalyst, etc.).

Metal complex catalytic systems are one of the most important classes of catalytic systems, both

for the polymerization and copolymerization of dienes. Therefore, the development of new effective catalytic systems, the study of the physicochemical laws of the formation and functioning of their active centers is of immense importance.

In the presented article, we have selected nickel-containing metal complex catalytic system for copolymerization of butadiene with ethylene. Various solutions of nickel-complexes and modifiers in aromatic solvents were prepared and their characteristics were established. Modifiers were selected as being more suitable for the conversion of both olefins and dienes [3-5]. The resulting systems were tested in the processes of copolymerization of ethylene with butadiene. Selection of non-metallocene nickel-containing complexes is due to the fact that they are more convenient and suitable for the transformation of dienes.

## 2. EXPERIMENTAL DETAILS AND METHODOLOGY

Schlenk's methods (operating in an inert atmosphere) were mainly used in experimental work. The common features of all working methods in an inert atmosphere were the removal of air from the reaction environment by vacuum, as well as the use of inert gases such as argon or nitrogen.

Ethylene copolymerization with butadiene was carried out in an autoclave made of stainless steel and designed for high pressure. The temperature in the reaction zone was maintained by an ultrathermostat and measured by a thermocouple of the recording device. The autoclave was equipped with a mixer, a jacket for cooling or heating, and nozzles for the entry of components, solvent, and aluminum-organic compound (AOC). The pressure in the reactor and the initial cylinder was monitored by a manometer. Prior to the process, the reactor was connected to a vacuum system, purified of oxygen and moisture under vacuum, at a temperature of 65-70°C for the duration of 1-2 hours. The reactor was then fed dry argon or nitrogen. The copolymerization of ethylene and butadiene was mainly carried out in an aromatic solvent environment. Preparations of solutions of catalyst components and delivery to the reactor were carried out under argon or nitrogen. The

components of the reaction mixture were introduced into the reactor as follows: the metal complex, AOC (methylalumoxane - MAO and/or  $\text{Et}_2\text{AlCl}$ ) solution, and finally the residual amount of solvent (through the dispenser), 10-15 minutes, at room temperature. At the end of the reaction, the active catalyst was decontaminated with a 10% alcohol solution of HCl acid. The waxy copolymers (CP) were dried under vacuum to constant weight after washing and filtration.

Ethylene – ( $\text{C}_2\text{H}_4$ ) used as a monomer (with a purity of 99.9%) was obtained from the pyrolysis process EP-300 in Sumgayit, Republic of Azerbaijan and dried with aluminum oxide.

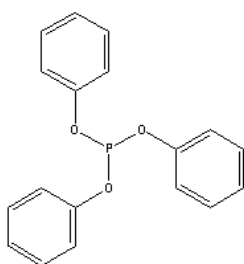
Butadiene - ( $\text{C}_4\text{H}_6$ ) used as a monomer (separated from fraction  $\text{C}_4$ ) was obtained from the pyrolysis process EP-300 in Sumgayit, Republic of Azerbaijan and dried with aluminum oxide.

Toluene, xylene were used as solvents for polymerization processes (99% purity, German production "Alfa Aesar"). Ethyl and isopropyl alcohols have been used as deactivators of catalytic systems after the polymerization of ethylene.

Nickel diethyldithiocarbamate [ $(\text{C}_2\text{H}_5)_2\text{NCSS}$ ] $_2\text{Ni}$  - (Ni-DTC) - synthesized by exchange reactions between sodium N,N- diethyldithiocarbamate and nickel dichloride, recrystallized from toluene solution [5]. Decomposition temperature - above  $250^\circ\text{C}$ .

As modifiers of the catalyst system triphenylphosphite (TPFt) and triphenylphosphine (TPFn) were obtained.

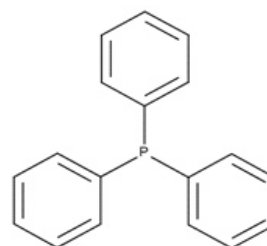
Triphenylphosphite - (TPFt)



was synthesized by the interaction of phenol and phosphorus trichloride. Freshly distilled phenol was loaded into a reactor equipped with a stirrer, dropping funnel, thermometer and reflux condenser, and phosphorus trichloride was

added dropwise at the melting point of phenol with stirring. After adding all of the phosphorus trichloride, the reaction mixture was stirred until the beginning of self-cooling and then gently heated to boiling. The reaction mixture was stirred at reflux until the reflux temperature remained constant. Then the reaction mixture was fractionated under vacuum. On re-distillation, a fraction with a boiling point of  $183^\circ\text{C}/1\text{ mm}$  was collected.

Triphenylphosphine - (TPFn)



was prepared in a three-necked flask with reflux condenser, dropping funnel and a mechanical stirrer. Phenylmagnesium bromide was obtained from magnesium and bromobenzene in 200 ml of absolute ether. Then, while cooling, an ethereal solution of phosphorus trichloride was dropped to the contents of the flask. The mixture was boiled for 10 minutes and decomposed with water. Triphenylphosphine was extracted with ether. The ether extracts were dried over calcined calcium chloride and, after distilling off the ether, were fractionated under vacuum. Trihexylphosphine and triheptylphosphine were prepared in a similar manner from hexyl bromide and heptyl bromide.

As a co-catalyst of the catalyst system,  $\text{Et}_2\text{AlCl}$  and  $\text{Et}_3\text{Al}$  of Aldrich Chemical Company were used.

Solutions of metal complexes and modifier in xylene in different concentrations were prepared. These solutions were analyzed in a «Nanosizer» spectrometer using the method of dynamic scattering of light [6,7]. This device was made in 2010, by "Horibo", Japan and is used in colloidal systems, emulsions, suspensions, micro heterogeneous catalytic systems to study the particle size (nm-micron), diffusion coefficient, with respect to their temperature dependence ( $5-70^\circ\text{C}$ ). The densities of metal complex and modifier solutions were measured on the DMA4500M device, by the ASTM D5002 method; the kinematic viscosities were measured on the

Stabinger SVM device, by the ASTM445 method, and the refractive indices were measured on the Abbemat500 device.

Molecular – weight distribution (MWD) of obtained products and the parameters were studied by size exclusion chromatography method using high performance “Kovo” (Czech Republic) liquid chromatograph, with a refractive index detector and UV– spectrophotometric ( $\lambda=254$  nm) detector. Two 3.3 mm-150 mm columns packed with the “Separon-SGX” stationary phase with a particle size of 7 mm and a porosity of 100 Å, were used. Dimethylformamide was used as an eluent (flow rate 0.3 ml/min, temperature 20-25°C). A calibration plot of log M versus VR in the range M = 2–100 - 102 was obtained using polyethylene glycol standards and transformed to the common dependence of fraction (%) of chains from their molecular weights. Calculations of the average molecular weights and MWD characteristics were conducted based on the data of size exclusion chromatographic analysis in accordance with the procedure described therein. Average molecular weights (Mw and Mn) were calculated using the following formulas:  $M_w = \sum M_i w_i$ ,  $M_n = 1/\sum w_i/M_i$ , where  $M_i$  is the molecular weight, corresponding to the  $i$ - slice of the chromatogram;  $w_i$  is the area fraction of  $i$  slice.

The thermodynamic parameters of the copolymers were determined by DSC on a Q-20 differential scanning calorimeter by Thermoelectron Corporation (USA), with a heating rate of 10 deg/min in an atmosphere of air or nitrogen.

The structure and composition of the obtained products were identified using IR- spectroscopy on a Spectrum One spectrophotometer, (Perkin Elmer, USA).

### 3. RESULTS AND DISCUSSION

Recent detailed studies of diethyldithiocarbamates of a number of transition metals have made it possible to reveal the effect of the metal atom on the crystal structure and the structure of the molecules of the complexes. A transition has been established from typical chelating compounds in the case of nickel and copper diethyldithiocarbamates to compounds in which the ligand, in addition to ring formation, also gives bridging bonds between neighboring molecules (zinc and cadmium diethyldithiocarbamates). With an increase in the

ordinal number of an element, there is an increase in the tendency towards the formation of linear hybridization, in the coordination of the metal [4].

High efficiency of nickel complexes in polymerization of butadiene has been determined in the researches carried out at the Institute of Petrochemical Processes named after academician Y.H.Mammadaliyev of Azerbaijan National Academy of Sciences (IPCP ANAS), for many years [3-5]. A scientific direction was created in the metal complex catalysis of the process of polymerization of dienes and the scientific basis for the creation of highly effective bifunctional catalysts-stabilizers, was developed. At present, research in this direction is being successfully continued.

#### 1. Copolymerization processes

In the presented article, we examine the known combined use of nickel complexes and modifiers. These systems have been tested in the copolymerization of ethylene with butadiene. The results obtained are shown in Table 1. The prepared catalytic systems (Table 1) provide for the formation of oligomeric and/or (co)polymer products having different molecular weights, mono/multimodality and/or narrow/wide MMD. The productivity of the catalytic system is 10-120 kg product/g Me · h<sup>-1</sup>. As evident (Table 1 [1,4,7]), ethylene is oligomerized in the presence of Ni-DTC and modifiers. When Ni-DTC is used in the catalytic system, butene-1 is selectively formed. The addition of modifiers leads to the formation of other higher oligomers (C<sub>4</sub>-C<sub>12</sub>) in accordance with the Schultz-Flori distribution. It should be noted that despite the acquisition of selectivity, activity is low in this case.

Polymerization of butadiene in the presence of N-DTC concludes with high activity:  $M_w / M_n = 1.8$ , in the microstructure contents of: 1.4-cis - 78%, 1.4 trans - 14%, and 1.2 - 8% (Table 1 [2,3]).

Taking into account the fact that modifying additives of the donor-acceptor type significantly affect both the polymerization rate and the properties of the obtained polymers, it was of particular interest to study their effect on the activity and selectivity of catalytic dithiosystems. TPFt and TPFn were used as such additives. With an increase in the P: Ni ratio from 1:1 to 3:1, the addition of these modifiers increases the (co) polymerization activity. During the polymerization

of butadiene, the content of 1,4-cis-units decreases, and the molecular weight remains almost unchanged.

The copolymerization of ethylene with butadiene (Table 1) leads to the production of wax-like copolymers in the presence of both Ni-DTC and modifiers, in which case MM<sup>3</sup>1000-6500, MWD=12-18.

Various analysis methods including IRS, DSC, were applied for identification of the structure of the synthesized products.

The synthesized (so)polymers were analyzed using IR spectroscopy. In this method, the degree of diversification, the ratio of asymmetric and symmetric methylene groups, the degree of saturation was determined. The IR spectra of copolymerization products revealed an absorption band at 1625 cm<sup>-1</sup>, corresponding to stretching vibrations of non-conjugated multiple C=C bonds, an intense absorption band in the region of 970 cm<sup>-1</sup>, characteristic of bending vibrations of the trans-C-H bond of disubstituted C=C, in the region 705 cm<sup>-1</sup>, corresponding to the cis-C-H bond of the disubstituted C=C.

As a rule, the composition of a copolymer usually has a wide distribution. Thus, some molecules or segments of a molecule may only have a few branches. However, there are many branches in other molecules or segments. This distribution is usually reflected in a wide range of melting temperatures. Additionally, the copolymerization of ethylene with butadiene, changes the linear structure of methylene rings. Due to this, the

degree of crystallization decreases, and the melting temperature decreases. In this case, a comparison of the melting temperature with PE shows that the melting point in the synthesized copolymers is low ((T<sub>m</sub>. = 110°C-120°C). In some cases, the melting point is very low, which indicates the formation of a completely amorphous copolymer.

### 1. Study of solutions of metal complexes and modifiers

Solutions of nickel complexes modifiers in aromatic solvents of various concentrations have been prepared. The parameters of the solutions are different, since they are prepared in different concentrations. A solution containing 0.2% Ni-DTC is characterized by: density at 20°C - 0,8675 g/sm<sup>3</sup>, kinematic viscosity at 20°C - 0,7471 mm<sup>2</sup>/sec., refraction at 20°C - 1,4964. A solution containing 0.1% Ni-DTC is characterized by: density at 20°C - 0,8349 g/sm<sup>3</sup>, kinematic viscosity at 20°C - 0,8550 mm<sup>2</sup>/sec., refraction at 20°C - 1,4900.

Their physical and chemical parameters have been determined. The results of the analysis of the prepared solutions by the method of dynamic scattering of light in the "Nanosizer" device are provided in Fig. 1.

The advantage of these catalytic systems is that they are highly soluble and compatible with the applied modifiers. They can be used in conjunction with aromatic solvents. As you can see, the distribution of particles in the solution is in the nanoscale region – median 13.7 nm.

**Table 1. Results of copolymerization processes of ethylene with butadiene in the presence of Ni-DTC. (Reaction conditions: time = 60 minutes, T = 25-90°C, P = 30-45 atm, [Me] = 10<sup>-4</sup> mol/l., Al:Me=150-2000, Al:Me=150-1000)**

No	modifier	monomers	AOC	Products
1	-	ethylene	Et <sub>3</sub> Al/Et <sub>2</sub> AlCl	butene-1
2	-	butadiene	Et <sub>2</sub> AlCl	PB
3	-	butadiene	Et <sub>3</sub> Al /Et <sub>2</sub> AlCl	PB
4	TPFt	ethylene	Et <sub>3</sub> Al/Et <sub>2</sub> AlCl	olefins
5	TPFt	butadiene	Et <sub>2</sub> AlCl	PB
6	TPFt	butadiene	Et <sub>3</sub> Al /Et <sub>2</sub> AlCl	PB
7	TPFn	ethylene	Et <sub>3</sub> Al/Et <sub>2</sub> AlCl	olefins
8	TPFn	butadiene	Et <sub>2</sub> AlCl	PB
9	TPFn	butadiene	Et <sub>3</sub> Al /Et <sub>2</sub> AlCl	PB
10	-	ethylene+ butadiene	Et <sub>3</sub> Al/Et <sub>2</sub> AlCl	CP
11	-	ethylene+butadiene	Et <sub>3</sub> Al /Et <sub>2</sub> AlCl	CP
12	TPFt	ethylene+butadiene	Et <sub>3</sub> Al /Et <sub>2</sub> AlCl	CP
13	TPFn	ethylene+butadiene	Et <sub>3</sub> Al /Et <sub>2</sub> AlCl	CP

Me\* - are the metals - nickel, cobalt, titanium contained in the metal complex

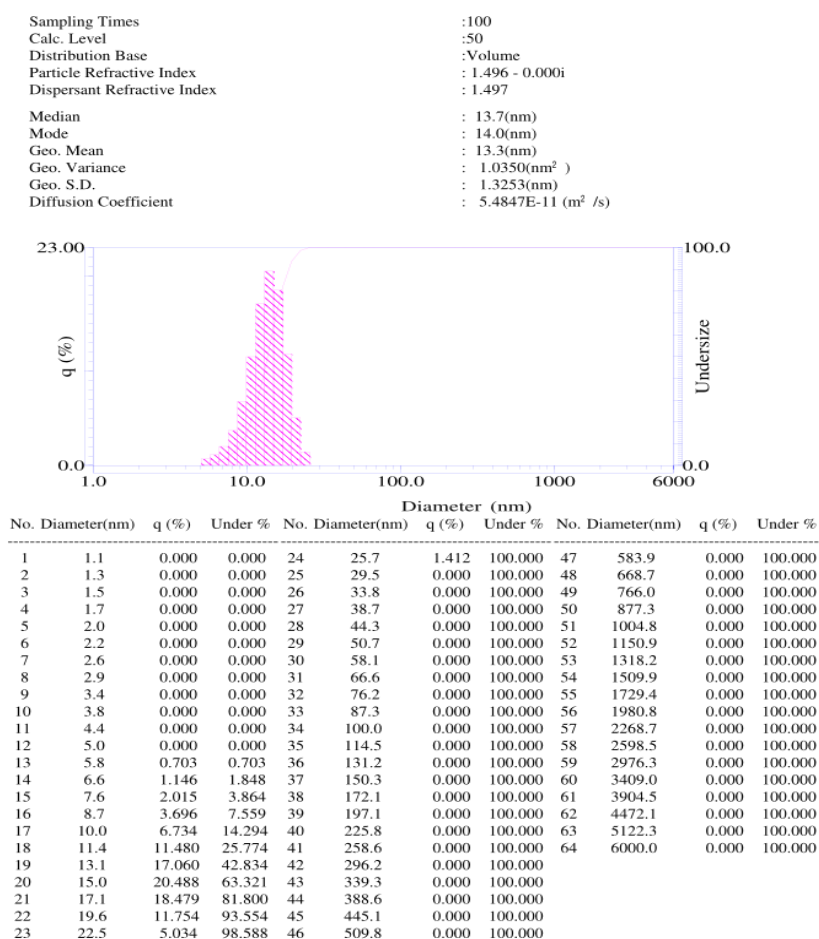


Fig. 1. Parameters of solution Ni-DTC, TPFT and TPFn

Dithiocarbamate complexes of nickel have been tested in the copolymerization of ethylene with butadiene. In combination with various modifiers and cocatalysts, various cooligomeric and copolymeric products were obtained in their presence. These products were characterized by various molecular, thermophysical, and spectroscopic parameters. The solubility of complexes of Ni-DTC, triphenylphosphite and triphenylphosphine was studied at various concentrations. It has been shown that these complexes can be easily used as homogeneous systems in liquid-phase cooligomerization and copolymerization of olefins and dienes. It is known that during polymerization in solutions under such ultrahomogenized conditions, the removal of heat from the reaction volumes, mixing and transportation of reaction products, the possibility of organizing continuous production and automating its control are greatly facilitated. Thus, it should be noted that, on the basis of research, effective catalytic systems have been developed that allow regulating

copolymerization processes with obtaining products from oligomers to high-molecular compounds with desired properties.

#### 4. CONCLUSIONS

It is known that the synthesis of copolymeric materials of the given structure is one of the most important areas of chemistry. It is important to control the parameters, in particular the molecular properties, of copolymers synthesized in both gas and liquid phase copolymerization. There are many scientific directions for this. One of the main directions is metal complex catalysis, which has ample opportunities for the synthesis of polymers with certain characteristics. The design of ligands, the choice of metals, organoaluminum compounds, and conditions of copolymerization allow achieving various important results. The choice of metal complex systems with the participation of various modifiers and ligands is of particular importance. The results of our studies indicate the possibility

of using such systems for the copolymerization of olefins and dienes. The results obtained will be useful for the synthesis of various copolymeric materials, including thermoplastics, elastomers, and other important products, as well as for the preliminary planning of a series of experiments in the future.

## DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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