
# SYNTHESES BASED ON THE TELOMERIZATION REACTION

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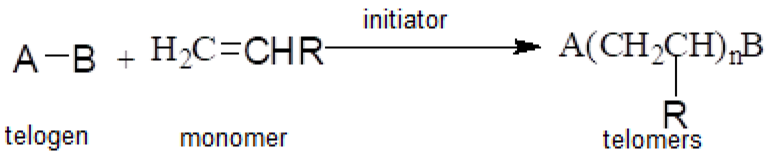
**ABSTRACT**

*This article explores the synthesis of chemical compounds through telomerization reactions. Telomerization is a chain process involving the interaction between low-molecular-weight telogens and monomers under catalytic conditions, leading to the formation of products referred to as telomers. The article specifically examines the telomerization of unsaturated compounds with alcohols, aldehydes, and peroxides, highlighting the roles of radical and ionic mechanisms involved in these reactions. The industrial significance of telomerization is discussed, particularly its applications in the synthesis of high-performance solvents, plasticizers, and lubricants, as supported by scientific literature. The results demonstrate the potential of this synthetic approach for enabling innovative applications in the chemical industry.*

Due to the rapid advancement of chemistry and innovative technologies, various methods for producing alcohols are currently being developed. Recent data indicate a growing demand for the industrial-scale production of these types of organic compounds [1].

The term telomerization is derived from the Greek words telos — meaning end or terminal, and meros — meaning part or segment. It describes a type of chain reaction in which repeating monomer units (M) are inserted between the two fragments of a compound X–Y (telogen), resulting in the formation of a homologous series of telomers with the general formula $X–M_n–Y$ (n = 2–40) [2].




One of the promising methods for utilizing natural and industrial gases in organic synthesis is the telomerization reaction. This approach enables the production of various mono-, bi-, and polyfunctional compounds of practical significance from simple olefins such as ethylene and propylene [3]. At present, telomerization reactions are employed in the manufacturing of synthetic disinfectants, as well as detergents, waxes, lubricants, varnishes, solvents, dielectrics, plasticizers, resins, and synthetic fibers [4].

Telomerization plays an important role in the advancement of chemical science. As the number of carbon atoms in the molecule of an aliphatic compound increases, the complexity of its synthesis rises sharply. As a result, only a limited number of compounds containing 15 or more carbon atoms are currently known. Existing experimental data indicate that telomerization remains a relatively underexplored area within organic chemistry [5].

Depending on the nature of the X-group, the telomerization reaction can proceed via coordination, free-radical, or ionic mechanisms. The general scheme of the telomerization reaction can be represented as follows:

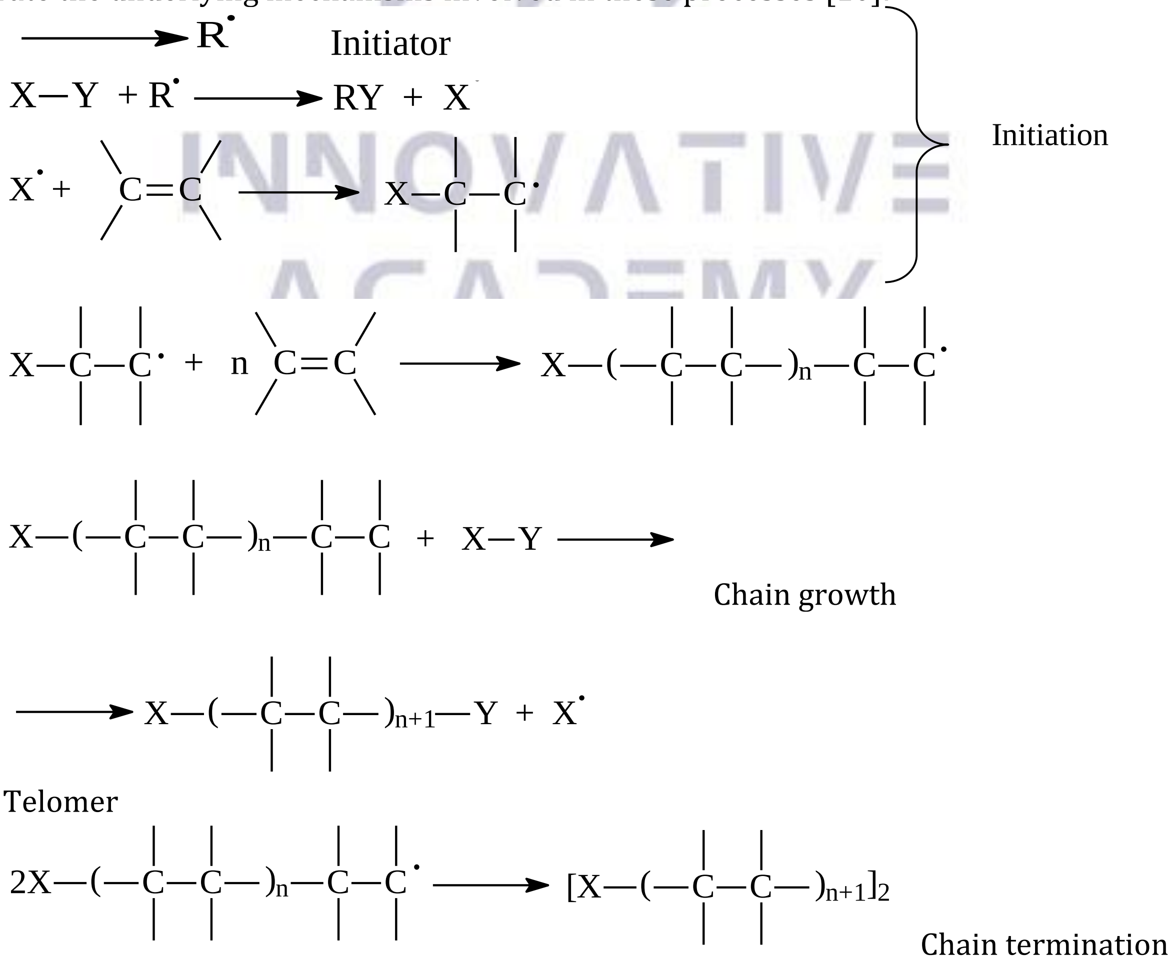
$nRCH = CH_2 + XY \rightarrow_{(initsiator)} X(RCHCH_2)_nY$

In this context, XY serves as the chain carrier in the reaction.

However, such generalized schemes do not necessarily imply that all studied telomerization reactions exhibit a chain character [6]. In cases where the X–Y bond is susceptible to homolytic cleavage, the telomerization reaction proceeds via a free radical mechanism. It is not appropriate to include compounds containing only C–F bonds in such reactions. Telomerization reactions involving aromatic compounds with non-activated C–N bonds are typically inefficient, and in the case of acetylenic homologs, telomerization is almost nonexistent [7]. Although C–H bonds in amino acids can participate in the reaction, C–N bonds generally do not undergo telomerization. In cyclic compounds, the reaction may proceed either with ring retention or ring opening [8].

Peroxides are the most commonly used initiators. Additionally, azo compounds, oxygen, and ultraviolet (UV) or gamma (γ) radiation can also initiate the telomerization reaction. Unsaturated compounds are most frequently used as monomers [9].

For radical telomerization reactions, the following schemes have been proposed to illustrate the underlying mechanisms involved in these processes [10]:



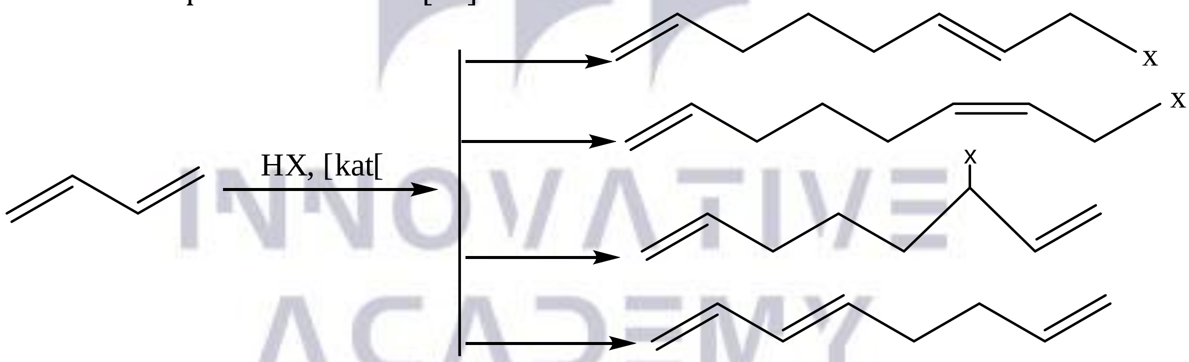
This scheme is not universally applicable to all reactions, as there are known telomerization reactions that do not conform to it. Additionally, the scheme does not account for the formation of by-products [11].

Numerous scientists have made significant contributions to the development of this field. For example, N. Semenov developed the theory of chain reactions; S. Medvedev and his colleagues proposed mechanisms of chain transfer; and S. Bagdasaryan investigated the mechanisms of initiation and inhibition in polymerization reactions. Their work has played an important role in advancing telomerization research [12].

N. Nesmeyanov and his students conducted a series of studies on the telomerization of olefins with carbon tetrachloride, chloroform, and silicon hydrides. The telomerization of ethylene with carbon tetrachloride was carried out for the first time. In 1948, American chemists R. Joyce, N. Hanford, and I. Harmon studied this reaction under pressure in the presence of benzoyl peroxide. They successfully isolated the reaction products containing between 3 and 9 carbon atoms and confirmed their structure as $[Cl(CH_2CH_2)_nCCl_3]$.

Subsequently, G. B. Ovakimyan and A. A. Beer developed and implemented a straightforward continuous method for synthesizing such compounds on an industrial scale. Research conducted by A. Karapetyan demonstrated that the composition of the telomer mixture is primarily determined by the molar ratio of ethylene and carbon tetrachloride fed into the reactor [13].

Takahashi and Smutny independently discovered the telomerization reaction of 1,3-butadiene. In this process, telomerization involves the dimerization of 1,3-butadiene through the addition of a telogen. The products of this reaction are referred to as telomers, and the reaction scheme is presented below [14].



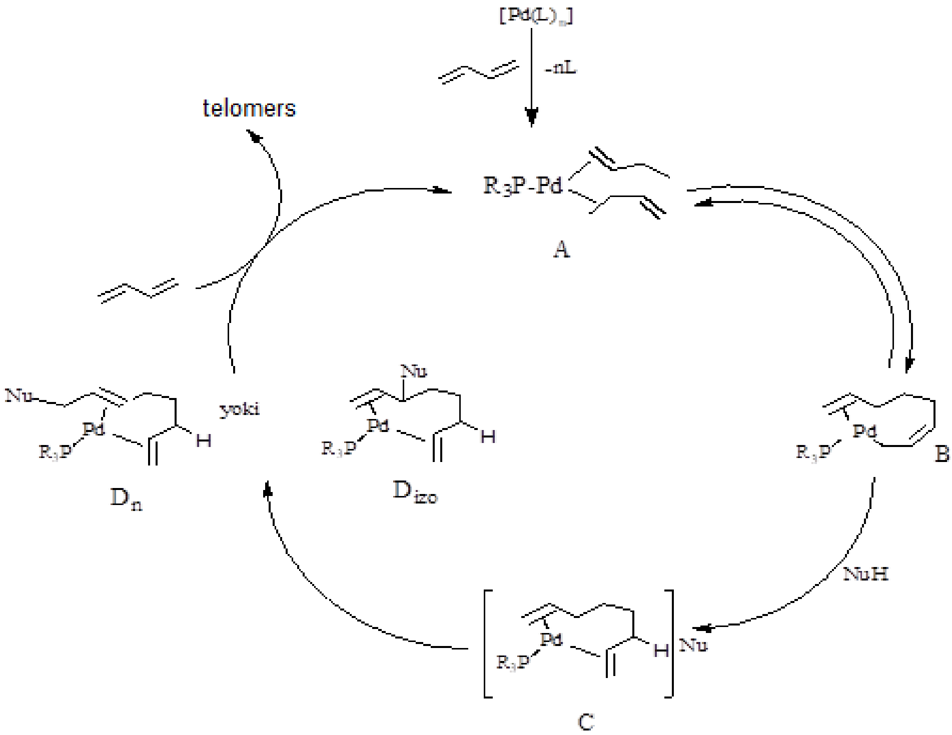

Products of the telomerization reaction of 1,3-butadiene

Multiple isomers can be formed in this reaction. In addition to 1,3-butadiene, other dienes, including cyclic dienes such as cyclopentadiene, can also be used. A wide range of compounds can serve as telogens, such as water, ammonia, alcohols, or acidic substances. When water is used as the telogen, unsaturated alcohols are produced [15].

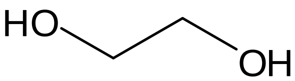
The Kuraray company has industrially produced 1-octanol at a scale of 5,000 tons per year, primarily using organometallic compounds of palladium and nickel as catalysts. In 2008, Dow Chemical initiated the industrial-scale production of 1-octene from butadiene in Tarragona. In this process, the telomerization of butadiene with methanol in the presence of a palladium catalyst yields 1-methoxy-2,7-octadiene, which is subsequently fully hydrogenated to 1-methoxyoctane. In a final step, 1-methoxyoctane is converted into 1-octene and methanol [16].

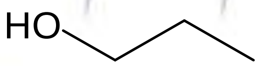
Regina Palkovits and her research team investigated the telomerization reactions of 1,3-butadiene with various alcohols using different catalytic systems. Palladium and phosphine were employed as catalysts in these reactions. Their research focused on the activity of Pd/phosphine systems in telomerization and their involvement in nucleophilic reactions, which contributed to advancing telomerization processes involving 1,3-butadiene and various nucleophiles. In their study, alcohols such as ethylene glycol, 1- and 2-propanol (1-PrOH, 2-

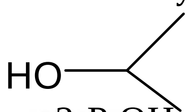
PrOH), 1,2- and 1,3-propanediol (1,2-PD, 1,3-PD), glycerol (Gly), and 1,2- and 1,4-butanediol (1,2-BD, 1,4-BD) were used as nucleophiles [17].

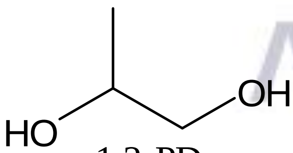


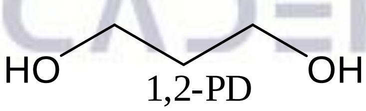

Telomerization reaction of 1,3-butadiene with palladium and nickel catalysts


EG

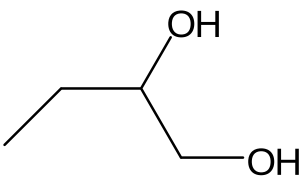

1-PrOH

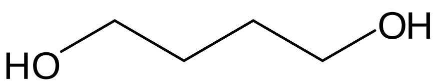

2-PrOH


1,2-PD

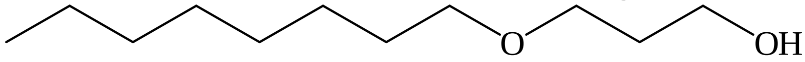

1,2-PD


Gly

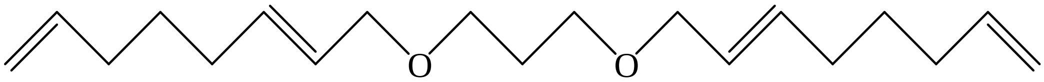

1,2-BD


1,4-BD

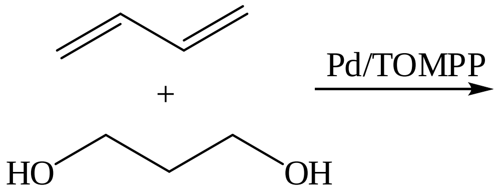
In this study, the telomerization of 1,3-butadiene with 1,3-propanediol (1,3-PD) resulted in the formation of the following products.

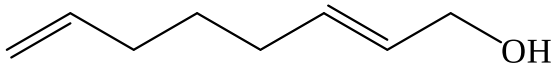



Oktadienilefir (1)

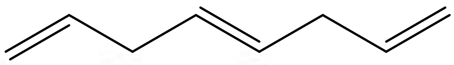



Bis-oktadienilefir (2)

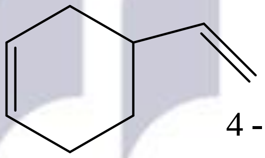



2,7 - oktadienol (5)



1,4,7 - oktatrien (3)



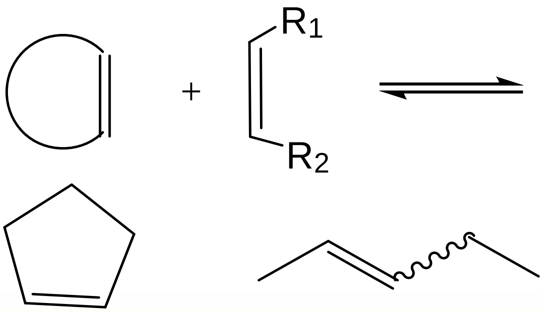
4 - vinilsiklogeksen (4)

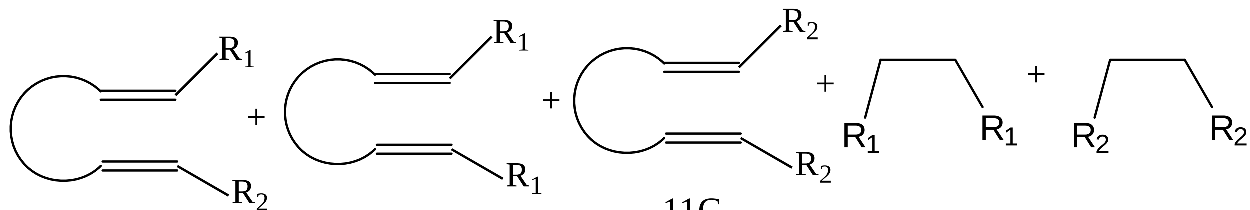
The products formed in this reaction include mono-telomers (octadienyl ethers) (1), di-telomers (bis-octadienyl ethers) (2), and 2,7-octadienol (5), which is obtained through the hydrolysis of the telomer products with water. Dimerization products such as 1,4,7-octatriene (3) and 4-vinylcyclohexene (4) are also formed. The telomerization of 1,3-butadiene with various alcohols and its interaction with diols has been studied using Pd/TOMPP catalysts [18].

Raw materials capable of undergoing telomerization—such as ethylene, other olefins, and their halogenated derivatives—enable the synthesis of highly functional mono- and bifunctional compounds, including acids. The halogen-substituted acids obtained through telomerization can be used for the synthesis of both saturated and unsaturated acids [19].

Several researchers—S. Bigot, J. Lai, I. Schweitzer, and M. Sauthier—have studied the telomerization of 1,3-butadiene with glycerol under aqueous biphasic conditions, focusing on the influence of reaction conditions on product yield. During the reaction, butadiene is continuously supplied and the pressure is kept constant. To improve the activity and selectivity of the resulting mono-, di-, and tri-telomers, various reaction parameters were investigated.

Y. Chuamin and his students conducted telomerization reactions involving cyclopentane and 2-pentene [20].






A. Rzhevsky, A. Topchiy, and their collaborators studied the telomerization of isoprene with methanol in the absence of a solvent, in the presence of heterocyclic palladium complexes. The telomerization processes of butadiene with arylamines in the presence of palladium complexes were investigated by R. Aripov, Ye. Ganieva, R. Izhberdina, R. Khusnutdinov, K. Khusnutdinova, and I. Abdurakhmanov. O.B. Penrhyn-Lowe and his students studied the radical telomerization reactions of ethylene glycol dimethacrylate, 1,6-hexanediol dimethacrylate, and 1,12-dodecanediol dimethacrylate. A. Bechkoff, M. Belbachir, B. Guyot, and B. Boutevin researched the telomerization of styrene with mercaptans to produce functional telomers of macromonomers with variable molecular masses [21].

Telomerization reactions are of significant practical importance in the production of macrocyclic lactones, ω-amino acids, high-carbon fatty acids, and other organic compounds. In the telomerization of ethylene, radical rearrangement has been extensively studied on carboxylic acids and their derivatives. However, little research has been conducted on the rearrangement during the telomerization of alcohols [22].

The article reviews various methods for synthesizing aliphatic alcohols and analyzes research conducted by leading scientists from major scientific centers and educational institutions worldwide. It covers both laboratory and industrial methods for synthesizing saturated alcohols, producing alcohols from unsaturated hydrocarbons, and synthesis reactions based on telomerization. It also discusses the achievements in alcohol synthesis, their chemical transformations, kinetics, production technologies, and application areas.

Furthermore, the influence of the nature, structure, number, and spatial configuration of radicals in starting materials, as well as the type, nature, and amount of solvents and catalysts used in the process, has been analyzed. Researchers worldwide have studied intermediate and by-products formed in these processes using various catalysts.

In conclusion, it can be stated that the synthesis of alcohols through telomerization and the development of industrial-scale production technologies have been extensively analyzed. The synthesis and large-scale production of such compounds—and the design of new organic substances with unique properties based on them—are identified as urgent scientific and practical issues.

Ethylene production through natural gas processing is of great importance. In these processes, ethane and other various hydrocarbons serve as the primary raw materials. Currently, most of the ethylene produced in our country is used for polyethylene synthesis. Additionally, ethylene can be used in the synthesis of cycloalkanes, valuable olefins, flotation reagents, technical cleaning agents, and the synthesis of synthetic fatty acids and alcohols.

The industrial-scale production of saturated alcohols from ethylene has great practical significance. One of the unconventional methods for obtaining necessary alcohols in the industry is the synthesis of higher alcohols from lower molecular weight alcohols via the telomerization reaction. The reaction of saturated alcohols with ethylene proceeds via a free radical telomerization mechanism. Initially, branching occurs in the carbon chain of the growing telomer, as the growing radical undergoes homolytic rearrangement. In this mechanism, various telomers are formed depending on the initial alcohol. Acetone was used as the catalyst in the telomerization reaction, while hydrogen peroxide and organic peroxides (tert-butyl peroxide (TBP), benzoyl peroxides) were used as initiators.

In this article, the telomerization process of ethylene with methanol is thoroughly analyzed. The reaction proceeds via a radical mechanism in the presence of hydrogen peroxide ($H_2O_2$). Acetone was used as the solvent. Within the scope of the telomerization reaction, the initiation, propagation, and termination stages occur at the molecular level. Additionally, the physicochemical properties, selectivity, and industrial applications of the resulting telomer products are discussed.

Telomerization is a chain radical process in which telomers with controlled molecular weight and well-defined structures are formed through the interaction of a monomer and a telogen. Unlike polymerization, this reaction results in low-molecular-weight products.

The ethylene molecule ($CH_2{=}CH_2$) possesses a pi-bond with high electron density, making it reactive toward radical attack. Methanol acts as an easily accessible proton donor and serves as the telogen. Hydrogen peroxide, chosen for initiation, is a strong oxidizing agent that functions as a radical initiator. Acetone, used as the solvent, adjusts the dielectric properties of the reaction medium and helps stabilize the radicals formed.

The radical mechanism of telomerization follows the conventional principles of chain reactions and proceeds through three main stages:

This article presents a detailed analysis of the telomerization process of ethylene with methanol.

The reaction was carried out via a radical mechanism in the presence of hydrogen peroxide ($H_2O_2$). Acetone was used as the solvent. Within the telomerization process, the initiation, propagation, and termination stages proceed at the molecular level. Additionally, the physicochemical properties, selectivity, and industrial applications of the telomer products were discussed.

Telomerization is a chain radical process in which telomers with a defined structure and controlled molecular mass are formed from a monomer and a telogen. Unlike polymerization, these reactions yield low molecular weight products. The ethylene molecule ($CH_2{=}CH_2$) possesses a π-bond with high electron density. Methanol, being a good proton donor, acts as a telogen. Hydrogen peroxide, chosen for initiation, is a strong oxidizing agent and serves as a radical-forming compound. Acetone, used as the solvent, adjusts the dielectric properties of the reaction medium and ensures the stability of radicals.

The radical mechanism of the telomerization reaction is based on the classical chain reaction principle and proceeds in three main stages:

Initiation:

Hydrogen peroxide decomposes in the presence of metal ions to form radicals:

$H_2O_2 \rightarrow 2\ HO\bullet$

The resulting hydroxyl radicals interact with methanol molecules to form methoxy radicals:

$HO\bullet + CH_3OH \rightarrow CH_3O\bullet + H_2O$

Propagation (Chain Growth):

The methoxy radical first adds to the ethylene molecule:

$CH_3O\bullet + CH_2{=}CH_2 \rightarrow CH_3O–CH_2CH_2\bullet$

This radical then reacts with additional ethylene molecules:

$CH_3O–CH_2CH_2\bullet + nCH_2{=}CH_2 \rightarrow CH_3O–(CH_2CH_2)_n–CH_2CH_2\bullet$

During this stage, the molecular weight of the product is relatively controlled—telogen presence limits chain length.

Termination:

The chain is terminated by a free hydrogen radical or another methanol molecule:

$CH_3O–(CH_2CH_2)_n–CH_2CH_2\bullet + H\bullet \rightarrow CH_3O–(CH_2CH_2)_n–CH_2CH_3$ or

$CH_3O–(CH_2CH_2)_n–CH_2CH_2\bullet + CH_3OH \rightarrow CH_3O–(CH_2CH_2)_n–CH_2CH_2OH + CH_3O\bullet$

This completes the active growth of the telomer molecule.

Physicochemical properties of telomer products — The general structure of the resulting telomers is $CH_3O-(CH_2CH_2)_n-X$, where X = H or OH. These products possess the following properties: relatively low boiling points (100–160°C), viscosity dependent on telomer chain length, high polarity enabling them to dissolve a wide range of inorganic and organic compounds, and good stability against light and oxygen—making them easy to store and transport.

Industrial applications:

Ethylene–methanol telomerization products are used as organic solvents, plasticizers, and lubricants in the following industrial sectors:

•Paints and coatings industry: Used as highly volatile solvents, especially for coating metal surfaces.

•Polymer production: Telomers are added as plasticizers.

•Agrochemicals: Used as solvents in the formulation of pesticides and herbicides.

•Lubricants: Incorporated into specialized oils for mechanisms operating in harsh environments.

The relevance of telomerization reactions has been increasing in recent years due to the growing demand for organic synthesis, environmentally safe technologies, and high-value-added products. Especially, the advantages of the ethylene–methanol system—its use of inexpensive and readily available raw materials, the ability to obtain products with high selectivity, and controlled molecular architecture—make this method widely applicable in practice.

Another important aspect is that methanol is a renewable feedstock (e.g., derived from biomass or synthesis gas), which brings the reaction closer to environmentally sustainable technologies. Ethylene, a major olefin extensively produced in the petrochemical industry, shows high reactivity in telomerization and helps reduce energy consumption.

Moreover, telomer products (e.g., polyethylene glycol ethers, solvents) are important intermediates in pharmaceuticals, cosmetics, polymers, and agrochemicals. This makes the process not only theoretically interesting but also a strategic technological link in global production chains.

Today, reactions that comply with the principles of sustainable chemistry, green chemistry, and waste-free technologies are of special interest. Telomerization falls into this category, as it proceeds under low pressure, relatively low temperature, uses water-generating initiators ($H_2O_2$), and yields selective products—significantly reducing industrial waste. Furthermore, its consideration as an alternative pathway to polymer synthesis, ability to generate flexible molecular architectures, and potential integration with nanotechnologies make it a highly relevant subject for scientific research.

Industrial Applications

The telomerization products of ethylene and methanol are used as organic solvents, plasticizers, and lubricants in various industrial sectors:

Paints and coatings industry: Utilized as highly volatile solvents, especially for coating metal surfaces.

Polymer production: Telomers are added as plasticizers to enhance flexibility.

Agrochemicals: Serve as solvents in the formulation of pesticides and herbicides.

Lubricants: Used in special lubricating oils for mechanisms operating in harsh environments.

The relevance of telomerization reactions has significantly increased in recent years due to the growing demand for organic synthesis, environmentally safe technologies, and the production of high value-added products. In particular, the advantages of the ethylene–methanol system—based on inexpensive and readily available feedstocks, the ability to obtain products with high selectivity and controlled properties—make this method highly applicable in practice.

An additional important factor is that methanol is a renewable feedstock (e.g., derived from biomass or synthesis gas), which aligns the reaction with environmentally sustainable technologies. Ethylene, a major olefin widely produced in the petrochemical industry, exhibits high reactivity in the telomerization process and contributes to reduced energy consumption.

Moreover, telomerization products (e.g., polyethylene glycol ethers, solvents) are important intermediates in the pharmaceutical, cosmetic, polymer, and agrochemical industries. This highlights the process not only as a subject of theoretical interest but also as a strategic technological link in global production chains.

Currently, reactions that comply with the principles of sustainable chemistry, green chemistry, and zero-waste technologies are attracting considerable attention. Telomerization belongs to this class of reactions, as it proceeds under low pressure, at relatively low temperatures, utilizes water-forming initiators (like $H_2O_2$), and yields highly selective products, thereby significantly reducing industrial waste. Additionally, its potential as an alternative route to polymer synthesis, ability to construct flexible molecular architectures, and compatibility with nanotechnological integration make it a highly relevant field for scientific research.

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