SCHEME OF ETHYLENE TELOMERIZATION REACTION

Khudayberganova Sevara Zokirjonovna
Tashkent State Technical University, Senior Lecturer

Abstract
During the telomerization reaction of ethylene with methyl alcohol, isopropyl alcohol is formed using a system consisting of hydrogen peroxide and acetone as a catalyst. Ethylene acts as a monomer, and methyl alcohol serves as a telogen. The process begins with the formation of telomers corresponding to the initial alcohol. The reaction follows a free radical mechanism, starting with the interaction of hydrogen peroxide with acetone.

**Keywords**. Ethylene, methanol, radical, telomer, telogen, acetone.

Introduction

The term telomerization derives from the Greek words telos (end, part) and meros (portion, share). It refers to a type of chain reaction where the repeating fragment of a monomer (M) is introduced between two fragments (X-Y) of a telogen molecule, resulting in a set of homologous telomers X-Mn-Y (n=2-40) [1].

One of the promising methods for using natural and industrial gases in organic synthesis is the telomerization reaction, which allows obtaining various mono-, bi-, and multifunctional compounds important for practical applications, based on the simplest olefins such as ethylene and propylene [2]. Currently, this reaction is used for the production of synthetic disinfectants, as well as for detergents, waxes, lubricants, paints, solvents, dielectrics, plasticizers, resins, and synthetic fibers [3].

The telomerization reaction plays an important role in the development of chemistry. As the number of carbon atoms in the molecule of aliphatic compounds increases, the difficulties in their synthesis increase sharply. Therefore, very few compounds containing 15 or more carbon atoms in the molecule are known. Existing experimental data show that the telomerization reaction is a less exploredfield of organic chemistry [4].

Depending on the nature of particle X, the telomerization reaction proceeds based on coordination, free radical, and ionic mechanisms. The telomerization reaction can be expressed by the following scheme.

$$nRCH = CH_2 + XY \rightarrow_{\text{(initiator)}} X(RCHCH_2)_nY$$
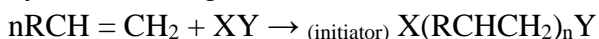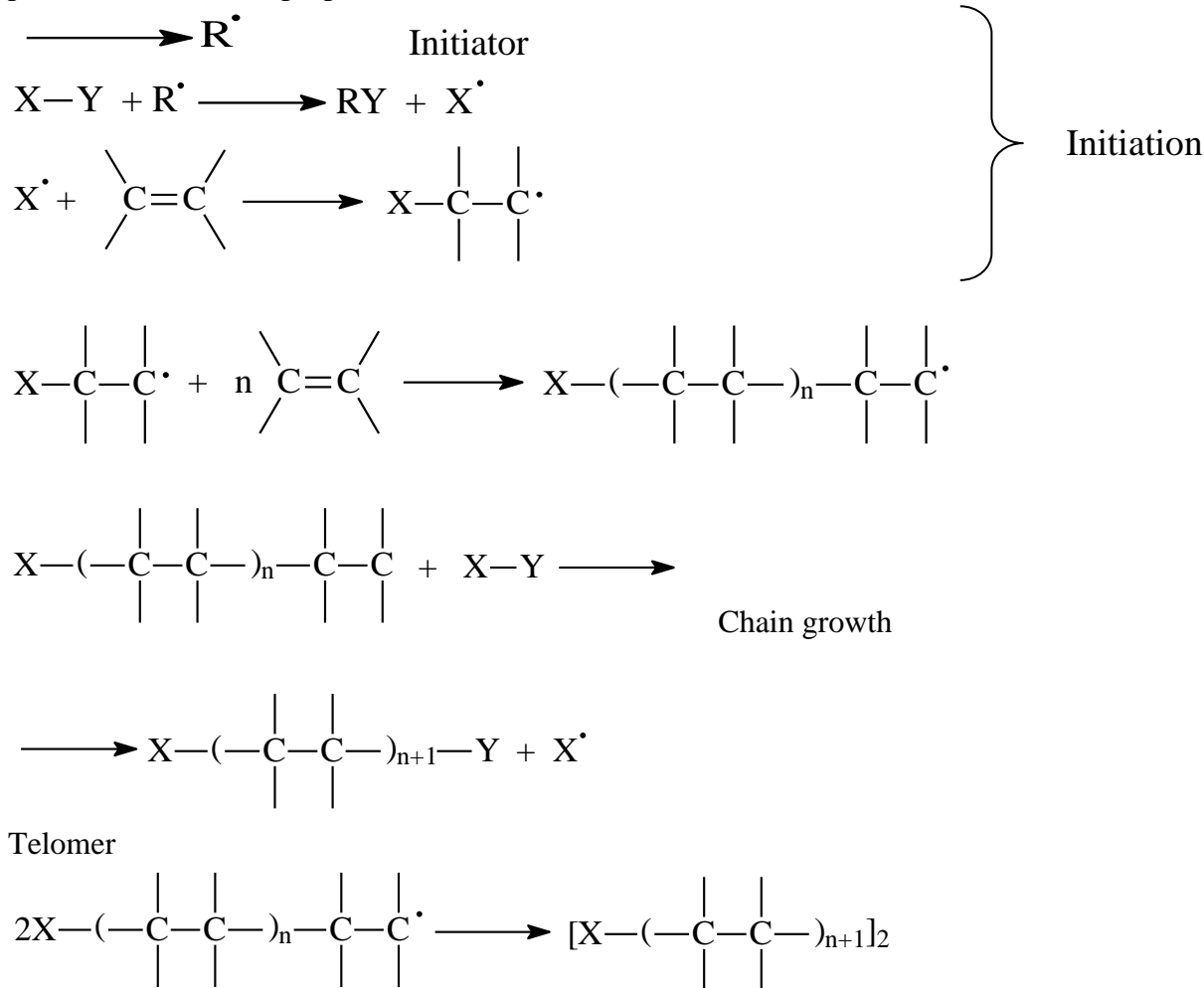
In this context, XY represents the carrier of the reaction chain. However, these types of schemes do not necessarily indicate that all studied telomerization reactions have a chain-like character. In substances prone to homolytic bond cleavage, the telomerization reaction proceeds based on the free radical mechanism. It would not be appropriate to include substances with C-F bonds in such reactions. Aromatic compounds with an unactivated C-N bond do not undergo telomerization reactions well, and telomerization is almost non-existent in acetylene homologs
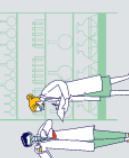
[5]. The C-H bonds in amino acids participate in the reaction, but telomerization does not occur with C-N bonds. In cyclic compounds, telomerization may occur with the opening and closing of the cycle [6].

Peroxides are the most commonly used compounds as initiators. Azocompounds, oxygen, and UV or γ-radiation can also ensure the occurrence of the telomerization reaction. Unsaturated compounds are frequently used as monomers [7].

For radical telomerization reactions, the following schemes, reflecting the mechanisms of these processes, have been proposed [8]:

$$\longrightarrow R^\bullet \qquad \text{Initiator}$$

$$X{-}Y + R^\bullet \longrightarrow RY + X^\bullet$$

$$X^\bullet + \;\; \overset{\diagdown}{\diagup}C{=}C\overset{\diagup}{\diagdown} \longrightarrow X{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{}^\bullet \qquad \right\} \text{ Initiation}$$

$$X{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{}^\bullet + \; n\; \overset{\diagdown}{\diagup}C{=}C\overset{\diagup}{\diagdown} \longrightarrow X{-}({-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-})_n{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{}^\bullet$$

$$X{-}({-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-})_n{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}} + \; X{-}Y \longrightarrow$$

Chain growth

$$\longrightarrow X{-}({-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-})_{n+1}{-}Y + X^\bullet$$

Telomer

$$2X{-}({-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-})_n{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{}^\bullet \longrightarrow [X{-}({-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-})_{n+1}]_2$$

Chain termination

This scheme is not universal for all reactions because telomerization reactions that do not conform to this scheme are also known. Moreover, the scheme does not indicate the formation of by-products [9].

Many scientists have contributed significantly to the development of this field. For example, N. Semenov developed the theory of chain reactions, S. Medvedev and colleagues proposed chain transfer mechanisms, and S. Bagdasaryan studied the initiation and inhibition mechanisms of polymerization reactions, contributing to the development of telomerization.

Web of Scientists and Scholars: Journal of Multidisciplinary Research
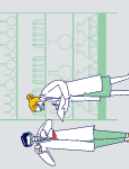
N. Nesmeyanov and his students conducted a series of studies on the telomerization reactions of olefins with carbon tetrachloride, chloroform, and silicon hydrides. For the first time, the telomerization reaction of ethylene and carbon tetrachloride was carried out. In 1948, American chemists R. Joyce, N. Hanford, and I. Harmon studied the telomerization reaction between ethylene and carbon tetrachloride under pressure in the presence of benzoyl peroxide. They isolated reaction products containing 3 to 9 carbon atoms in the molecule and demonstrated that they have the following structure: $[Cl(CH_2CH_2)nCcl_3]$.

Subsequently, G. B. Ovakimyan and A. A. Beer demonstrated, through their studies, the possibility of developing and implementing a simple continuous industrial method for synthesizing such compounds. A. Karapetyan's research revealed that the composition of the telomer mixture largely depends on the molar ratio of ethylene and carbon tetrachloride introduced into the reactor [10].

Takahashi and Smutny independently discovered the telomerization reaction of 1,3-butadiene. In this reaction, telomerization represents the dimerization reaction of 1,3-butadiene with the addition of a telogen. The products of this reaction are called telomers, and the process scheme is shown below [11].
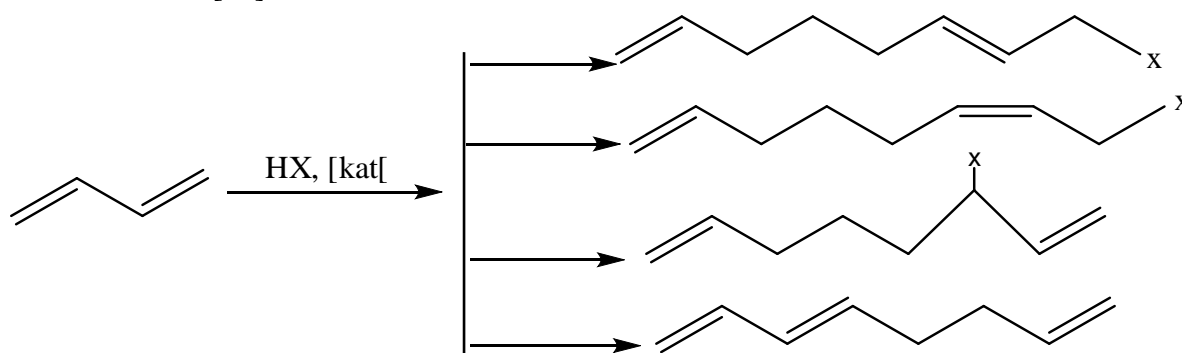

Telomerization Products of 1,3-Butadiene

In this process, several isomers can be formed. Besides 1,3-butadiene, other dienes or cyclic dienes such as cyclopentadiene are also utilized. Various compounds, such as water, ammonia, alcohols, or acidic compounds, can be used as telogens. When water is used, unsaturated alcohols are obtained [11].

The Kuraray company has produced octanol-1 on an industrial scale (5,000 tons per year), using palladium and nickel organometallic compounds as catalysts. The production of octene-1 from butadiene was initiated in 2008 in Tarragona by Dow Chemical. In the presence of a palladium catalyst, telomerization of butadiene with methanol produces 1-methoxy-2,7-octadiene, which is then fully hydrogenated to 1-methoxyoctane in a subsequent step. Finally, octene-1 and methanol are obtained from 1-methoxyoctane [12].
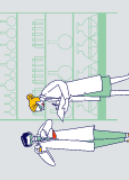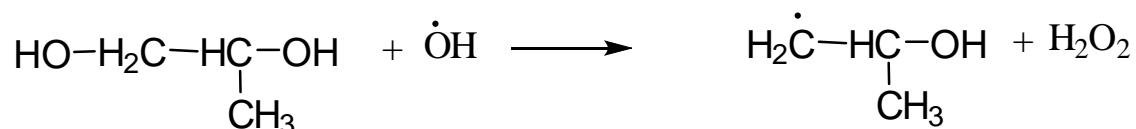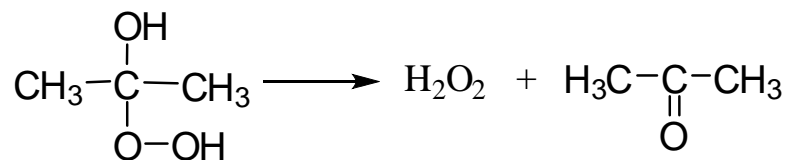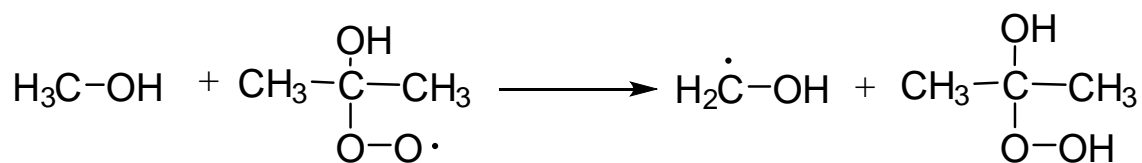
Regina Palkovis and her students studied the telomerization reactions of 1,3-butadiene with various alcohols in the presence of different catalysts. Palladium and phosphine were used as catalysts. This research focused on the activity of the telomerization process involving new Pd/phosphine systems and their nucleophilic reactions. It subsequently contributed to the development of the telomerization process of 1,3-butadiene with various nucleophiles. In this

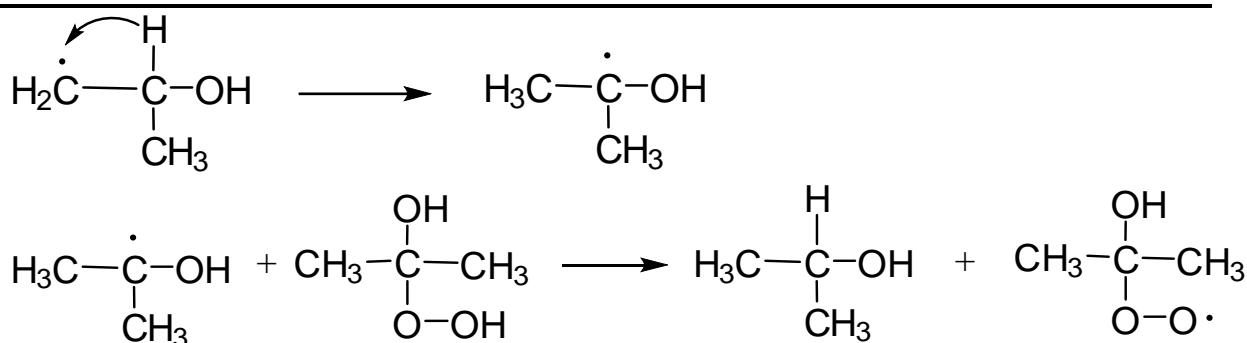study, nucleophiles included alcohols such as ethylene glycol, 1- and 2-propanol (1-PrOH, 2-PrOH), 1,2- and 1,3-propanediol (1,2-PD, 1,3-PD), glycerol (Gly), and 1,2- and 1,4-butanediol (1,2-BD, 1,4-BD) [13].

Etilene's telomerization with methyl alcohol (methanol) to form isopropyl alcohol can be represented by the following reaction:

$$H_3C-OH + H_2C=CH_2 \xrightarrow{H_2O_2 \, , \, CH_3\text{-}C(O)\text{-}CH_3} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$
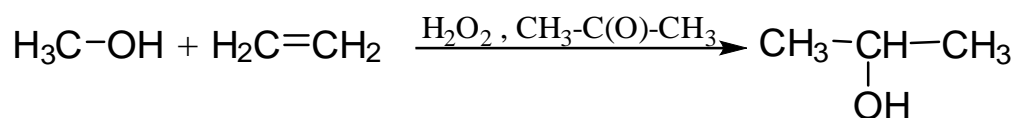
The process you describe follows a free radical mechanism, where hydrogen peroxide and acetone form a catalytic system, while ethylene serves as the monomer and methyl alcohol acts as the telogen. The reaction begins with the formation of telogens corresponding to the initial alcohol. Here's a step-by-step outline of the mechanism:

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + H_2O_2 \longrightarrow CH_3-\underset{\underset{O-OH}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

$$CH_3-\underset{\underset{O-OH}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 + H_2O_2 \longrightarrow H_2O + \dot{O}H + CH_3-\underset{\underset{O-O\cdot}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

$$H_3C-OH + \dot{O}H \longrightarrow H_2\dot{C}-OH + H_2O$$

$$H_2C=CH_2 + \dot{O}H \longrightarrow H_2\dot{C}-H_2C-OH$$

$$H_2\dot{C}-OH + H_2\dot{C}-H_2C-OH \longrightarrow HO-H_2C-\underset{\underset{CH_3}{|}}{HC}-OH$$

$$H_3C-OH + CH_3-\underset{\underset{O-O\cdot}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \longrightarrow H_2\dot{C}-OH + CH_3-\underset{\underset{O-OH}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

$$CH_3-\underset{\underset{O-OH}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \longrightarrow H_2O_2 + H_3C-\underset{\underset{O}{\|}}{C}-CH_3$$

$$HO-H_2C-\underset{\underset{CH_3}{|}}{HC}-OH + \dot{O}H \longrightarrow H_2\dot{C}-\underset{\underset{CH_3}{|}}{HC}-OH + H_2O_2$$
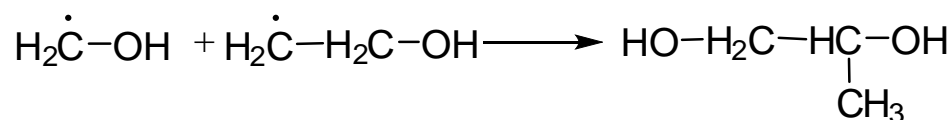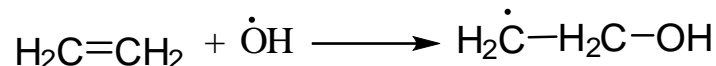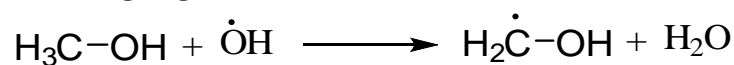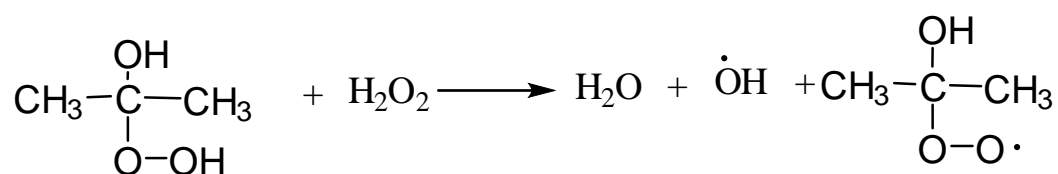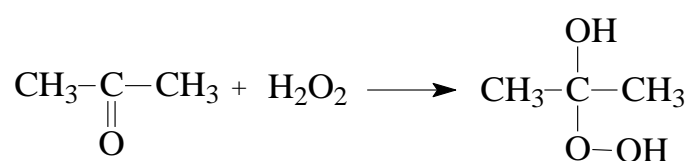
The general mechanism of the oxidation reaction in the presence of peroxides in this process is as follows: initial stage – radical formation: Acetone reacts with hydrogen peroxide, producing radical particles. At this stage, the peroxide bonds break, forming active radicals. Next stage – radical addition: The formed radicals interact with active groups of other organic molecules. During this process, carbonyl groups (C=O) or hydroxyl groups (OH) are oxidized, leading to the formation of new peroxide or hydroxyl radicals. Branching stage: Active radicals continue chain reactions, resulting in the formation of several oxidation products. In this stage, alcohols (-OH), diol groups (two hydroxyl groups), and other complex compounds are formed. Final stage – radical recombination: Radical particles combine to form stable products. As the final products of the oxidation, alcohols and peroxide compounds appear. During the oxidation process, the structure of the organic compound changes, and new covalent bonds are formed.The driving force of the reaction is the high reactivity of peroxides.

The synthesized isopropyl alcohol was used as an extractant-solvent for purifying sulfur from mechanical impurities in the Mubarek Gas Processing Plant. The process involved adding 13.3 liters of isopropyl alcohol to 4 kg of technical sulfur in a 20-liter autoclave, mixing for 1 hour, extracting, and filtering. The extract was distilled, yielding 3.7 kg of purified sulfur. Additionally, 12.8 liters of recovered isopropyl alcohol were recommended for reuse as an extractant.

REFERENCES

1. Р.И. Хуснутдинов, Н.А. Щаднева, Т.М. Ошнякова, У.М. Джемилев. Теломеризация z,z-циклооктадиена с галогенметанами, катализируемая соединениями хрома, меди и молибдена в присутствии воды // Нефтехимия, 2011, Том № 51(6). – С. 443.

2. James M. Takacs, Edward C. Lawson, and, Francis Clement. On the Nature of the Catalytic Palladium-Mediated Elimination of Allylic Carbonates and Acetates To Form 1,3-Dienes // Journal of the American Chemical Society, 1997, Volume 119(25). – pp. 5956-5957.

3. К.Н. Ершукова, З.Д. Абрамов, А.В. Сучкова, М.В. Быков, Д.С. Суслов. Теломеризация изопрена с диэтиламином в присутствии палладиевых катализаторов // Сборник статей Международной научно-практической конференции им. Д.И. Менделеева, 2022, Том 1. – С. 140-142.

4. С.А. Ржевский, М.А. Топчий, М.С. Нечаев, А.Ф. Асаченко. Теломеризация изопрена с метанолом катализируемая N-гетероциклическими карбеновыми комплексами палладия (II) // Химия и химическая технология в XXI веке : Материалы XXII Международной научно-практической конференции студентов и молодых ученых имени выдающихся химиков Л.П. Кулёва и Н.М. Кижнера, 2021, Том 1. – С. 235-236.

5. Теломеризация изопрена со спиртами, катализируемая карбеновыми комплексами палладия(II), без использования растворителя / М. А. Топчий, А. А. Агешина, С. А. Ржевский // Известия Академии наук. Серия химическая, 2022, Том № 5. – С. 940-945.

6. Ji Yang, Peng Wang, Helfried Neumann, Ralf Jackstell, Matthias Beller. Industrially applied and relevant transformations of 1,3-butadiene using homogeneous catalysts // Industrial Chemistry & Materials, 2023, Volume 1(2). – pp. 155-174.

7. Yasuhisa Matsukawa, Junji Mizukado, Heng-dao Quan, Masanori Tamura, Akira Sekiya. Palladium(0)-Catalyzed Hydroalkoxylation of Hexafluoropropene: Synthesis of Hydrofluoroethers under Neutral Conditions // Angewandte Chemie International Edition, 2005, Volume 44(7). – pp. 1128-1130.

8. M. Maji, D. Panja, I. Borthakur, S. Kundu. Recent advances in sustainable synthesis of N-heterocycles following acceptorless dehydrogenative coupling protocol using alcohols // Organic Chemistry Frontiers, 2021, Volume № 8(11). – pp. 2673-2709.

9. И.П. Ким, Д.П. Кирюхин, В.Г.Курявый, В.М. Бузник. Колесникова, Дифференциальный термогравиметрический анализ продуктов радиационно-химической теломеризации тетрафторэтилена в ацетоне // Химия высоких энергий, 2009, Том № 43(1). – С. 25-31.

10. И.П. Ким, А. Ф. Шестаков. Образование коллоидных растворов и гелей при радиационно-химической теломеризации тетрафторэтилена в ацетоне // Химия высоких энергий, 2009, Том 43, № 6. – С. 516-522.

11. Г.А. Кичигина, Д.П. Кирюхин, П.П. Кущ, А.И. Большаков. Радиационная теломеризация тетрафторэтилена в растворе хлористого бутила // Химия высоких энергий, 2011, Том № 45(1). – С. 40-45.

12. И.П. Ким. Молекулярно-массовое распределение олигомеров в продуктах теломеризации тетрафторэтилена в различных растворителях // Химия высоких энергий, 2011, Том № 45(5). – С. 399-405.

13. Г.А. Кичигина, П.П. Кущ, А.М. Колесникова, Д.П. Кирюхин. Особенности радиационной теломеризации и свойств теломеров тетрафторэтилена в хлорсодержащих растворителях // Химия высоких энергий, 2011, Том № 45(5). – С. 431-436.

Web of Scientists and Scholars: Journal of Multidisciplinary Research