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Hydrogen peroxide as a chain transfer agent in the radical diene polymerization

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Analysis of chain termination in the radical polymerization of dienes in solutions of alcohols initiated by hydrogen peroxide has shown that chain termination is accomplished by chain transfer to initiator, rather than by recombination of macroradicals. This conclusion is made on the basis of calculations of the rates of chain termination by both paths, carried out using our own and published data on the rate constants of macroradical reactions and comparing them with data on the functionality of oligodienes by hydroxyl groups. The problem of reactivity of hydroxyl radicals formed in the chain transfer on hydrogen peroxide molecule is discussed. The reaction rate of the hydroxyl radical with double bond of the oligomer, which proceeds with the formation of allylic radical in the chain, is estimated from the rate constants of similar reactions in methyl methacrylate and α -methyl styrene. The peculiarity of this reaction is determined by the high activity of hydroxyl radicals and nonselectivity of their interactions in the system, which leads to the chain transfer to the oligomer. Thus, in this system, hydrogen peroxide acts simultaneously as a polymerization initiator and a chain transfer agent, which leads to the termination of macroradicals with forming a terminal hydroxyl group.

Keywords: diene radical polymerization, HTPB; hydrogen peroxide, chain termination, chain transfer.

Hydrogen peroxide (HP) as the initiator of radical polymerization is very promising because of its potential to replace common initiators such as peroxides and hydroperoxides [1]. It has a number of advantages over these initiators: low cost, ecological friendliness, low molecular weight, which allows reducing its consumption as initiator. In addition, HP introduces terminal hydroxyl groups into polymers, which is very important for the production of reactive oligomers, in particular hydroxyl-containing oligodienes (HTPB).

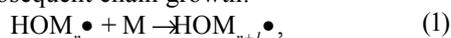
In spite of the dignities of HP as initiator, its use in the radical polymerization has been widely used only at the polymerization of water soluble monomers. In this case initiation comes true by hydroxyl radicals, generated by oxidation-reduction systems of the Fenton reagent type [2]. This mechanism will not be realized in non-aqueous media with low polarity. It is considered [3, p. 37], that at heating there is a homolytic decomposition of HP on two hydroxyl radicals. However, this process at the temperatures of polymerization (at least to 150 °C) does not take place because of high bond dissociation energy of O-O in the HP molecule [4, 5]. Before [6, 7] the mechanism of the generation of the primary radicals in the diene-HP-solvent triple complex was proposed. This mechanism requires that the chain termination is accomplished not by recombination of macroradicals, as occurs in the polymerization of dienes with other initiators, but by chain transfer to the initiator HP. In carrying out the polymerization

in alcoholic solutions, oligomers with two terminal hydroxyl groups are formed, as at recombination of macroradicals, however, every fourth hydroxyl group is introduced into oligodiene by a hydroxyl-containing fragment of an alcohol. Such a mechanism is realized only when polymerization is initiated by two different radicals, one of which is alcoholic, and chain transfer of both macroradicals to HP with the formation of terminal hydroxyl groups. This mechanism was confirmed by the polymerization of isoprene in labeled ^{14}C alcohols [6]. In this paper, we present evidence of this mechanism, based on the analysis of kinetic data in the polymerization of isoprene, obtained by us and given in the literature.

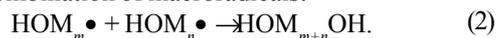
Chain transfer to an initiator in radical polymerization is known [8, p. 62–63]. Thus, diacyl peroxides are prone to decompose when they are attacked by a radical. The attack goes to one of oxygen atoms of the peroxide group. This reaction is especially important at high monomer conversions when the ratio of an initiator concentration to a monomer increases, as well as in the oligomerization reactions, when the high ratio is initially set. In some cases, for example, in the polymerization of styrene with benzoyl peroxide, this pathway is the main way of chain termination. It was established in [9] that in the case of photopolymerization of vinyl acetate at 20 °C in the presence of HP transfer to HP is dominated in the chain termination reaction. Kirsch et al. [10, 11] showed that the chain termination in the radical polymerization of vinyl pyrrolidone

in the isopropyl alcohol (IPA) solution initiated by dinitrile of azo-bis-isobutyric acid, in the presence of HP in the polymerization system, is linear, that is, there is no recombination of macroradicals. This property of HP bases on its action as a regulator of molecular weight in the radical polymerization of vinyl pyrrolidone [12]. The authors of [9–11] believe that the chain transfer to HP is carried out by abstracting a hydrogen atom to form an inactive perhydroxy radical. In our paper [13] it was shown that in the polymerization of butadiene, the transfer to HP with both macroradicals and hydroxyl radicals is enthalpically much more advantageous to peroxide bond than abstraction of a hydrogen atom. The value of the standard enthalpy of the reaction of polybutadiene macroradicals with HP is 19,7 kJ / mol when a hydrogen atom is abstracted, and -107,9 kJ / mol when the hydroxyl group is done through peroxide bond.

Macroradicals are formed upon initiation of polymerization and subsequent chain growth:



and are consumed in reactions (2) and (3). The chain termination during the radical polymerization of dienes with typical radical initiators is carried out almost completely by the recombination of macroradicals:



The chain transfer reaction to the HP takes the form:



We assume that the chain termination in this system is carried out only by the second way (equation (3)). We note at once that the chain transfer to other components of this system is unimportant: the chain transfer constants at 90 °C to monomer $C_{tr} = 0,6 \cdot 10^{-4}$ (the value of the chain transfer constant to dienes is close to this value for styrene ([14, p. 192]) and to IPA ($C_{tr} = 3 \cdot 10^{-4}$) are insignificant and do not have a noticeable effect on the molecular parameters of oligodienes. The transfer reaction to polymer at low monomer conversions are neglected. The values of interest to us the rate constants for isoprene polymerization are given in Table 1.

The rate constant of the chain transfer by the macroradical to HP k_{tr} was calculated from the data of Ref. [16] by the value of the chain transfer constant to polymer in the isoprene polymerization $C_{tr} = k_{tr} / k_p = 0,215$. The calculations given below were carried out for the polymerization of isoprene under the following conditions: $[M] = 3,60 \text{ mol l}^{-1}$, $[I] = 0,60 \text{ mol l}^{-1}$, solvent IPA, and temperature 90 °C. The initial velocity $V_0 = 3,576 \cdot 10^{-5} \text{ mol l}^{-1} \cdot \text{s}^{-1}$ is taken

from our work on polymerization of isoprene at 90 °C in IPA solution [17, Table 2].

The reaction rates (1–3) are:

- chain propagation

$$V_p = k_p [M][P\bullet] \quad (4)$$

- chain termination by macroradical recombination:

$$V_t = k_r [P\bullet]^2 \quad (5)$$

- chain termination by chain transfer by macroradical to initiator HP:

$$V_{tr} = k_{tr} [I][P\bullet]. \quad (6)$$

Here, $[M]$, $[I]$, $[P\bullet]$ are the concentrations of monomer, initiator and macroradicals, k_p , k_r and k_{tr} are the rate constants of the chain propagation, the chain termination by recombination and chain transfer to HP.

Let us compare the rates of the parallel reactions of macroradicals: the chain termination by recombination (5) and the chain termination by transfer to HP (6). To do this, it is necessary to know the concentration of macroradicals $[P\bullet]$. It can be found from the initiation rate w_p , which was found from the radical polymerization equation:

$$V_0 = \frac{k_p}{k_t^{1/2}} \cdot w_i^{1/2} \cdot [M]. \quad (7)$$

Substituting the experimentally found value $V_0 = 3,576 \cdot 10^{-5} \text{ mol l}^{-1} \cdot \text{s}^{-1}$ at $[M] = 3,60 \text{ mol l}^{-1}$, and taking

(Table 1) $\frac{k_p}{k_t^{1/2}} = \frac{164,50}{(1,33 \cdot 10^8)^{1/2}} = 0,0143$ we find $w_i =$

$4,825 \cdot 10^{-7} \text{ mol l}^{-1} \cdot \text{s}^{-1}$. Since the initiation rate in the stationary state is equal to the termination rate, and the termination occurs parallel by the recombination of macroradicals V_r and the chain transfer to initiator V_{tr} , then:

$$w_i = V_r + V_{tr} = k_r [P\bullet]^2 + k_{tr} [I][P\bullet]. \quad (8)$$

Substituting the known values, we obtain the quadratic equation for $[P\bullet]$:

$$4,825 \cdot 10^{-7} = 1,33 \cdot 10^8 [P\bullet]^2 + 35,440,6 [P\bullet],$$

from which we find the concentration of macroradicals $[P\bullet] = 2,02 \cdot 10^{-8} \text{ mol l}^{-1}$.

Now you can find the both termination rates. The chain termination by chain transfer to HP:

$$V_{tr} = 35,4 \times 2,02 \cdot 10^{-8} \times 0,6 = 4,284 \cdot 10^{-7},$$

and the chain termination by macroradical combination:

$$V_t = 1,33 \cdot 10^8 \times (2,02 \cdot 10^{-8})^2 = 5,410 \cdot 10^{-8}.$$

The ratio $V_{tr} / V_t = 4,306 \cdot 10^{-7} / 5,465 \cdot 10^{-8} = 7,92$, i.e. the portion of the chain termination by the chain transfer to HP is $7,92 / 8,92 = 0,89$. It follows from the calculation that the chain termination by recombination of macroradicals

Table 1. The reaction rate constants for polymerization of isoprene at 90 °C

Reaction	Rate constant	Value, $\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	Literature
(1)	Chain propagation	$k_p = 164,50$	[15]
(2)	Chain termination by macroradical recombination	$k_r = 1,33 \cdot 10^8$	
(3)	Chain transfer to HP*	$k_{tr} = 0,215 \times 164,50 = 35,4$	[16]

*120 °C

Table 2. Rate constants of hydroxyl radical reactions at 90 °C

Reaction	Substance	Rate constant, $l \text{ mol}^{-1} \text{ s}^{-1}$	Literature
1	Isoprene	$41.2 \cdot 10^9$	18
2	Oligoisoprene	$2.47 \cdot 10^9$	Our calculation
3	HP	$2.7 \cdot 10^7$	19
4	IPA	$3.30 \cdot 10^9$	20

is not predominant, in contrast to the polymerization of dienes with other initiators. Although this calculation is approximate due to the approximate evaluation of the transfer constant to HP k_{tr} , and non-ideal character of polymerization, the basic conclusion about the role of chain transfer to initiator is beyond doubt.

With the detected fraction of the chain termination by chain transfer to HP, the functionality by the label should be somewhat greater than 0,5, since some of macroradicals will join together, giving the functionality of the macromolecules by label equal to 1. However, the high concentration of HP and the low concentration of macroradicals (their ratio is $0,6 / 2,02 \cdot 10^{-8} \approx 3,0 \cdot 10^7$) leads to the fact that the macroradicals react with HP, not having time to meet each other. In addition, the extremely high the chain transfer constant to HP (almost 400 times higher than to methanol and 120 times higher than that to tert-pentanol containing the methine unit [16]) makes the reaction with HP even more probable.

The question of the fate of the hydroxyl radicals formed in reaction (3) arises. These radicals can attack any of the molecules present in the system: monomer, oligomer, initiator HP, solvent IPA. The rate constants of the corresponding reactions are given in Table. 2.

The rate constant of the interaction of a hydroxyl radical with polyisoprene is unknown. It proceeds mainly with the abstraction of a hydrogen atom from the α -methylene group with respect to a double bond (mainly in the vinyl units) to form water and an allyl radical [13]. In α -methylstyrene and MMA, when the hydroxyl radical reacts with the methyl group, a hydrogen abstraction rate constant with formation of an allyl radical is about 6% of the rate constant of the addition of the radical to a double bond [21]. For polyisoprene, the reaction from the data of this work is: $k_{tr} = 0,06 \cdot 41,2 \cdot 10^9 = 2,47 \cdot 10^9 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. From the data of Table 2 a hydroxyl radical in the gas phase (and in the first approximation in solution [8, p. 26]) reacts with isoprene, oligomer, IPA and HP with the rate constants ratio 3800: 230: 300: 1, respectively. It follows that the reaction of the hydroxyl radical induced decomposition of HP does not take place. The hydroxyl radicals should mainly be spent in the reactions with the monomer (88 %), oligomer (~ 5 %) and IPA (~ 7 %). Indeed, the chain transfer reaction to IPA by attacking by the hydroxyl radical goes to a very low degree: it turns out to be only about 2 % of the product of this reaction acetone. So, formed on

the reaction (3) the hydroxyl radicals should primarily be spent to reinitiate the polymerization by reaction with remaining monomer. In this case, two free hydroxyl radicals must remain of each three HP molecules (one HP molecule goes to initiate two initial chains, two others react with macroradicals). If both hydroxyl radicals are spent for reinitiation, the number of labels should be not 1 of 4, but 1 of 6, that is, the number-average functionality by the label should be not 0,5, but 0,33. Since the experiment with labeled alcohols reliably showed the first value, it must be recognized that the hydroxyl radicals, which formed after the chain termination on HP, are spent not on reinitiation, but on other reactions, possibly on the oxidation of the components and on the chain transfer to oligomer. This is confirmed by low efficiency of initiation in this process: for HP this value is 0,2–0,3 [22]. A hydroxyl radical, being very active and non-specific chemically, is limited in diffusion. On this occasion, Denisov writes: "A hydroxyl radical lives for a very short time because of its high chemical activity and therefore can not migrate to a sufficiently large distance" [23, p.67]. According to Denisov, the time of his life, is $6 \cdot 10^{-9} \text{ s}$, which is comparable with the amplitude of rapid vibrations of CH_2 -groups in polyethylene. Therefore, the object of his attack may be each molecule that is nearby, and the above ratio is not realized. The number of attacks of the hydroxyl radical is determined only by the partial, that is, by the molar concentration of monomer, initiator and alcohol, not by the rate constants with these substances. In the initial mixture, they are 3,6; 0,6 and 7,9 mol l^{-1} ; with the conversion the concentration of monomer and initiator decrease, the alcohol concentration practically remains constant, and the concentration of oligomer increases. After conversion of monomer of 50 %, a rapid increase in the oligomer functionality begins [24]. Apparently, the reaction of chain transfer to polymer by hydroxyl radicals formed at termination of macroradicals on HP is predominant at high conversions of the monomer.

Thus, the experimental data and the model calculations given above show that the chain termination in the diene-HP-IPA system is carried out by chain transfer carried out by macroradicals to an initiator HP. This conclusion requires a in-depth study of the chain transfer reactions in this specific system where HP acts as initiator and the chain transfer agent simultaneously.

Literature

1. *Boiko V.P., Grishchenko V.K.* Peroksid vodoroda v himii kauchuka, *Khim. prom. Ukraine*, 2011, no. 3: 65-79 (in Russian).
2. *Sychev A.Ya., Duka G.G.* Fundamental and applied aspects of homogeneous catalysis by metal complexes. Oxide and peroxide systems. In 2 parts, Chisinau: Information Center of the Chisinau State University, 2002. P. I: 442; P. II: 336 (in Russian).
3. *Entelis S.G., Evreinov V.V., Kuzaev A.I.* Reaktsionnosposobnyie oligomeryi, Moscow, 1985: 304 (in Russian).
4. Himiya i tehnologiya perekisi vodoroda; *G.A. Seryshev*, Ed. Leningrad: Khimiya, 1984: 200 (in Russian).
5. *Walling Ch.* Free Radicals in Solution. London: John Wiley & Sons, 1957: 631.
6. *Grishchenko V.K., Boiko V.P., Svistova E.I., Yatsimirskaya T.S., Valuev V.I., Dmitrieva T.S.* Hydrogen-Peroxide-Initiated Polymerization of Isoprene in Alcohol Solutions, *J. Appl. Polym. Sci.*, 1992, **46**, no. 12: 2081-2087. <https://doi.org/10.1002/app.1992.070461203>
7. *Boiko V.P., Grishchenko V.K.* The Influence of Solvent on the Isoprene Polymerization Initiated with Hydrogen Peroxide, *Kautschuk Gummi Kunststoffe*, 2009, **62**, no. 9: 546-549.
8. *Moad G., Solomon D.H.* The Chemistry of Radical Polymerization. Elsevier, 2006: 639.
9. *Abuin E.B., Lissi E.A., Avaria L.* Effect of pH on the Behavior of Hydrogen Peroxide as an Inhibitor or Chain Transfer, *J. Polym. Sci.: Polym. Letter*, 1988, **26**, no. 12: 501-503. <https://doi.org/10.1002/pol.1988.140261202>
10. *Shtamm E.V., Skurlatov Yu.I., Karaputadze T.M., Kirsh Yu.E., Purmal' A.P.* Opredelenie absolutnyih znachenii konstant skorosti rosta i obryiva pri polimerizatsii N-vinil-pirrolidona v vodnom rastvore metodom vraschayuschegosya sektora, *Vysokomolekul. soedineniya. Ser. B*, 1980, **22**, no. 6: 420-424 (in Russian).
11. *Karaputadze T.M., Shumsky V.I., Skurlatov Yu.I., Kirsh Yu.E.* Radikalnaya polimerizatsiya vinilpirrolidona v prisutstvii perekisi vodoroda v razlichnyih rastvoritelyah, *Vysokomolekul. soedineniya. Ser. B*, 1982, **24**, no. 4: 305-309 (in Russian).
12. *Kirsh Yu.E., Karaputadze T.M., Kochergin A.P., Bairamov Yu.Yu., Shumsky V.I., Skurlatov Yu.I., Ermolaev, Sus' T.N., Kirsanov A.T., Rodionov V.G.* Sposob polucheniya nizkomolekulyarnyih gomo- ili sopolimerov N-vinillaktamov. – Sert. 755800 USSR. Cl. 3 C 08 F 26/10. – Filled. 05.05.78; Publ. 15.08.80. *Bull. NO. 30* (in Russian).
13. *Boiko V.P.* Termohimicheskiy analiz reaktsiy peredachi pri oligomerizatsii dienov v prisutstvii peroksida vodovoda, *Vysokomolekul. soedineniya. Ser. A*, 2005, **47**, no. 12: 2081-2087 (in Russian).
14. *Oudian G.* Basics of polymer chemistry. Moscow: Mir, 1974: 614 (in Russian).
15. *Gobran R.H., Berenbaum M.B., Tobolsky A.V.* J. Bulk Polymerization of Isoprene: Kinetic Constants from the Dead-End Theory. *Polym. Sci.*, 1960, **46**, no. 161: 431-440. <https://doi.org/10.1002/pol.1960.1204614812>
16. *Brosse J.-C., Legeay G., Lenain J.-C., Bonnier M.* Synthese par voie radicalaire de polymers a extremités hydroxyées, 6. Etude des reactions de transfer. *Makromol. Chem.*, 1978, **179**, no. 1: 75-85. <https://doi.org/10.1002/macp.1978.021790108>
17. *Boiko V.P., Grishchenko V.K., Makitra R.G., Midyanina G.G., Pal'chikova E.Ya.* Korrelyatsionnaya zavisimost nachalnoy skorosti polimerizatsii izoprena, initsirovannoy peroksidom vodoroda, ot tipa rastvoritelya. *Polymer. Journ*, 2013, **33**, no. 1: 83-87 (in Russian).
18. *Atkinson R.* *Chem. Rev.*, 1985, **85**, no. 1: 69-201.
19. *Crowell R.A., Lian R., Sauer M.C., Oulianov D.A., Schrob I.A.* Geminate recombination of hydroxyl radicals generated in 200 nm photodissociation of aqueous hydrogen peroxide, *Chem. Phys. Lett.*, 2004, **383**, no. 5-6: 481-485. <https://doi.org/10.1016/j.cplett.2003.11.062>
20. *Overend R., Paraskevopoulos G.* Rates of OH Radical Reactions. 4. Reactions with Methanol, Ethanol, 1-Propanol, and 2-Propanol at 296 K, *J. Phys. Chem.*, 1978, **82**, no. 4: 1329. <https://doi.org/10.1021/j100501a001>
21. *Grant R.D., Rizzardo E., Solomon D.H.* Reactions of Hydroxyl Radical with Polymerizable Olefins, *J. Chem. Soc. Perkin Trans. II*, 1985: 379-384. <https://doi.org/10.1039/p29850000379>
22. *Spirin Yu.L., Grishchenko V.K., Kochetova G.I.* O mehanizme razlozheniya perekisi vodoroda v organicheskikh rastvoritelyah, *Theor. Exper. Chem.*, 1972, **8**, no. 4: 532-538 (in Russian).
23. *Denisov E.T.* Okislenie i destrukttsiya karbotsepynih polimerov. Leningrad: Khimiya, 1990: 288 (in Russian).
24. *Dmitrieva T.S., Valuev V.I., Fraishtadt V.Ya., Medova R.V.* Vzaimosvyaz molekulyarno-massovogo raspredeleniya i usloviy sinteza oligobutadienov, poluchennyih na perekisi vodoroda, *Prom. SK*, 1984, no. 11: 4-6 (in Russian).

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Пероксид водню як агент передачі ланцюга в реакції полімеризації дієнів

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Аналіз реакції обриву ланцюгів у радикальній полімеризації дієнів в розчинах спиртів, ініційованої пероксидом водню, показав, що обрив ланцюгів здійснюється передачею ланцюга на ініціатор, а не рекомбінацією макрорадикалів. Цей висновок зроблено на підставі розрахунків швидкостей обриву ланцюга обома шляхами, проведених з використанням власних і літературних даних по константах швидкостей реакцій макрорадикалів і порівняння їх з даними функціональності олігодієнів по гідроксильних групах. Обговорено питання реакційної здатності гідроксильних радикалів, що утворюються в акті передачі ланцюга на молекулу пероксиду водню. Швидкість реакції гідроксильного радикала з подвійним зв'язком олігомеру, яка відбувається з утворенням алільного радикала в ланцюзі, оцінена по константах швидкостей аналогічних реакцій в метилметакрилаті і α -метилстиролі. Особливість цієї реакції визначається високою активністю гідроксильних радикалів і неселективних їх взаємодій у системі, що приводить до протікання передачі ланцюга на олігомер. Отже, в цій системі пероксид водню виступає одночасно в ролі ініціатора полімеризації і агента передачі ланцюга, який приводить до обриву макрорадикалів з утворенням кінцевої гідроксильної групи.

Ключові слова: радикальна полімеризація дієнів, НТРВ; пероксид водню, обрив ланцюга, передача ланцюга.

Пероксид водорода как агент передачи цепи в реакции полимеризации диенов

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Анализ реакции обрыва цепей в радикальной полимеризации диенов в растворах спиртов, иницированной пероксидом водорода, показал, что обрыв цепей осуществляется передачей цепи на инициатор, а не рекомбинацией макрорадикалов. Этот вывод сделан на основании расчетов скоростей обрыва цепи обоими путями, проведенных с использованием собственных и литературных данных по константам скоростей реакций макрорадикалов и сравнения их с данными по функциональности олигодиенов по гидроксильным группам. Обсужден вопрос реакционной способности гидроксильных радикалов, образующихся в акте передачи цепи на молекулу пероксида водорода. Скорость реакции гидроксильного радикала с двойной связью олигомера, которая протекает с образованием аллильного радикала в цепи, оценена по константам скоростей аналогичных реакций в метилметакрилате и α -метилстироле. Особенность этой реакции определяется высокой активностью гидроксильных радикалов и неселективностью их взаимодействий в системе, что приводит к протеканию передачи цепи на олигомер. Таким образом, в данной системе пероксид водорода выступает одновременно в роли инициатора полимеризации и агента передачи цепи, которой приводит к обрыву макрорадикалов с образованием концевой гидроксильной группы.

Ключевые слова: радикальная полимеризация диенов, НТРВ; пероксид водорода, обрыв цепи, передача цепи.