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REVIEWS

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## Synthesis and Use of Hydrogenated Polymers

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**Abstract**—Specific features of homogeneous, heterogeneous, and nanoheterogeneous catalysis in hydrogenation of polymers and the advantages and drawbacks of various catalytic systems are considered. Differences in hydrogenation of polymers and monomers are discussed. Specific features of the behavior of polymer molecules, complicating the heterogeneous catalysis, are noted, such as diffusion of macromolecules into catalyst pores, conformational limitations, and rheology of polymer solutions. The main catalytic systems studied in polymer hydrogenation are listed. A separate section deals with hydrogenless hydrogenation of polymers. The properties and application fields of hydrogenated polymers are analyzed. Promising directions of studying the catalysis of hydrogenation of macromolecular compounds are outlined.

**Keywords:** polymer hydrogenation, hydrogenated butadiene–acrylonitrile rubber, polyvinylcyclohexane, nanoheterogeneous catalysis, homogeneous catalysis

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### INTRODUCTION

Hydrogenation of C=C double bonds and, in some cases, of aromatic rings in polymer molecules opens broad possibilities for preparing modified polymers exhibiting enhanced resistance to oxidants (oxygen, ozone), heat, ionizing and UV radiation, and petroleum products [1, 2]. Such hydrogenated polymers exhibit enhanced levels of such mechanical properties as tensile strength, elongation at break, tensile elastic modulus, spinnability from melt, and wear resistance. Therefore, hydrogenated polymers are demanded in petroleum, aerospace, and military industry and nuclear power engineering, and also as materials for Arctic conditions [3, 4] and as additives to lubricants [5].

Beyond Russia, hydrogenated polymers are produced by Zeon (Japan, butadiene–acrylonitrile rubber (BNR), trade name Zetpol), ARLANXEO (Germany, butadiene–acrylonitrile rubber, trade name THERBAN), KRATON (the United States, styrene copolymer, trade name KRATON G), Shell (styrene copolymer used as an additive to oils), etc. On the whole, hydrogenation is performed with butadiene–acrylonitrile [4, 6], buta-

diene–styrene (BSR) [7], and butadiene–isoprene [5] rubbers, polybutadiene [8], polystyrene [9], ketone–formaldehyde resins [10–13], silyl-substituted butadienes [14], polyphenylsilapentanes [15], and petroleum polymeric and indene–coumarone resins [16–18]. Either C=C bonds only or C=C bonds and aromatic rings can be hydrogenated. In hydrogenation of ketone–formaldehyde resins, saturation of double bonds is accompanied by slight deoxygenation.

Hydrogenation of various polymers is a subject of reviews [19, 20]; detailed review [2] considers hydrogenation catalysts and properties of hydrogenated polymers, and review [4], hydrogenation of butadiene–acrylonitrile rubbers. Review [21] deals with catalysts of hydrogenation of petroleum polymeric resins. Because in the past two decades more effective catalysts, new directions in catalysis, and new approaches to studying the polymer characteristics and reaction mechanisms have been developed, in this review we analyze and summarize the modern data on catalysis of hydrogenation of macromolecular compounds and on the properties and use of hydrogenated polymers.

## POLYMER HYDROGENATION CATALYSTS

Three groups of polymer hydrogenation processes can be distinguished: heterogeneous and homogeneous catalysis and noncatalytic hydrogenless processes. Catalysis in the dispersed phase by metal and sulfide nanoparticles (“colloidal catalysis” in accordance with the terminology suggested in [2]), i.e., nanoheterogeneous catalysis [22, 23] can be conventionally classed with heterogeneous processes. In this review, nanoheterogeneous catalysts will be considered separately from heterogeneous catalysts because of specific features of the behavior of macromolecules in porous and nonporous systems.

### *Heterogeneous Catalysis*

The advantages of heterogeneous catalysis over homogeneous catalysis are simple separation of the catalyst from the reaction products, no introduction of catalyst fragments into polymer chains, and larger possibilities of commercialization [20]. Hydrogenation of polymers differs from that of low-molecular-mass compounds because of limited mass transfer and influence exerted on the process by the molecular mass and structure of the macromolecule, by the solvent, by the solution rheology, and by conformational transformations of the chain [2, 8, 19, 24–30]. In other words, hydrogenation of polymers is influenced, along with thermobaric factors, also by the following factors: mass transfer, support type and morphology, polymer type and mean molecular mass, kind of solvent, and adsorption of macromolecules on active sites [28].

Diffusion factors in polymer hydrogenation are primarily associated with limitation of the diffusion of macromolecules into catalyst pores. Limitations of the diffusion of macromolecules in solution to the surface and limitation of the gas–liquid mass transfer can be readily lifted by increasing the stirring rate or diluting the solution [25]. The hydrogenation decelerates with an increase in the molecular mass. The diffusion limitations can be characterized by the parameter  $\lambda$  (ratio of the polymer coil diameter in a specific solution to the pore diameter) [27]. In the case of polystyrene hydrogenation, aromatic rings are completely hydrogenated at  $\lambda < 0.3$ , whereas at  $\lambda = 1.14$  the conversion of the aromatic rings under the same conditions is as low as 10% [27]. The degree of hydrogenation becomes lower than 100% at  $\lambda > 0.35$ , which is associated with the need

for deformation of the polymer chain for the diffusion into pores. Correspondingly, at a certain value of  $\lambda$  the hydrogenation becomes impossible because of diffusion limitations. Furthermore, long chains of high-molecular-mass polymers are characterized by low mobility [4]. This fact accounts for a drastic decrease in the hydrogenation rate on reaching certain molecular mass, observed by Ness et al. [26] in hydrogenation of polystyrene.

Even when active sites occur on the catalyst surface, adsorption of long chains onto them in one step is impossible, and more conformational transformations are required for complete hydrogenation of a high-molecular-mass polymer [26]. Thus, the reaction rate will be determined by the sum of the time of the hydrogen addition to double bonds and aromatic rings and the time of conformational transformations of the chains.

Along with diffusion limitations and entropy limitations to the adsorption on the surface, the affinity of the polymer molecule for active sites of the catalyst plays an important role. As demonstrated by the example of the polybutadiene hydrogenation on Pd/CaCO<sub>3</sub> [8], a large number of conformational transformations can occur in one adsorption step, with the degree of hydrogenation reaching ~85%. This is followed by desorption due to a decrease in the affinity of the molecule to the active sites and to the competing action of molecules that have not yet underwent hydrogenation. In addition, conformational transformations of partially saturated polymers occur more slowly because of their more rigid structure, which is noted, in particular, for the conversion of *cis*-polybutadiene to polyethylene [19]. The remaining ~15% of the unsaturated fragments undergo hydrogenation more slowly upon repeated adsorption.

The adsorption on active sites, probability of steric hindrance, and ease of conformational transformations are influenced also by the structure of the polymer molecule. For example, in styrene–butadiene copolymer, *trans*-1,4-fragments are hydrogenated more slowly and with higher activation energy compared to vinyl-1,2-fragments [29] because of better accessibility of active sites to the latter fragments. Naturally, aromatic rings are hydrogenated still more slowly. The conversion of olefin fragments, compared to the conversion of aromatic fragments, depends on the molecular mass of the polymer to a lesser extent [29].

The polymer globule size and, correspondingly, the value of  $\lambda$  depend on the solvent and on the polymer solution concentration. On the one hand, in a “good” solvent the polymer coils are unrolled, the conformational transformations are facilitated, and the chains become more accessible. This also favors inhibition of the chain degradation, as demonstrated in [30] by the example of the polystyrene hydrogenation on Pd/BaSO<sub>4</sub>. Addition of a “good” solvent, tetrahydrofuran, to a “bad” solvent, cyclohexane, inhibits the chain degradation, making the chains more accessible to hydrogenation and facilitating the diffusion of the molecules from the pores. On the other hand, as reported by Shirai et al. [24], the degree of hydrogenation of butadiene–acrylonitrile rubber in acetone (“good” solvent) is lower than in carbon tetrachloride (“bad” solvent). This is caused by straightening of polymer chains in acetone, which allows them to penetrate into pores, but only the polymer chain segment that penetrated into a pore is hydrogenated, and this fraction is minor. On the other hand, a compact coil (diameter 35–77 Å) penetrates into a pore completely if the pore diameter is larger than the coil diameter. Thus, the effect exerted by the solvent on the hydrogenation is ambiguous and is fully determined by the value of  $\lambda$  for the given system.

The solvent also influences the difference  $x_s$  between the energies of the interaction of solvent and polymer molecules with the catalyst surface [8]. Variation of the solvent composition allows control of the degree of hydrogenation in one adsorption step. It becomes possible to selectively hydrogenate only olefin fragments in styrene–diene copolymers by using an aromatic solvent, which is useful, e.g., for the synthesis of thickening additives to oils [5]. For example, the use of toluene instead of cyclohexane leads to a considerable decrease in the rate of hydrogenation of aromatic rings in the styrene–butadiene block copolymer without affecting the rate of hydrogenation of the double bonds [29]. Apparently, this fact is due to competition of toluene molecules and aromatic rings of the polymer for the active sites.

The following values of the pore diameter are reported [31] to be optimum for hydrogenation of polymers of different molecular masses: >200 kDa, 3000–4000 Å; <100 kDa, 300–700 Å. However, it is clear from the above data that the solvent should be chosen in combination with a specific support, because the ratio of the diameters of the polymer coil and pores, rather than their absolute values, is the decisive factor.

Along with the morphology, the support should also meet some other requirements. It should have no acid properties because of the risk of the chain degradation [4] and should be selective when it is necessary to hydrogenate only olefin fragments in styrene copolymers or butadiene–acrylonitrile rubbers. It is known that the pore size influences the conversion of C=C bonds and aromatic rings differently. C=C bonds can be hydrogenated on active sites located in pore issues [29]. Supports with narrower pores are suitable for hydrogenation of double bonds, whereas aromatic rings are hydrogenated on coarsely porous supports. Therefore, the use of finely porous supports (pore diameter <500 Å) opens the possibility of selective hydrogenation of double bonds only [32]. The conversion of aromatic rings largely depends also on the metal particle size: The larger the metal particle is, the higher is the probability of the arrangement of the whole coil on it in one adsorption step.

The characteristics of catalysts and conditions for hydrogenation of different polymers are given in [2]. Palladium, nickel, platinum, and, more seldom, rhodium and ruthenium are used as hydrogenating metals, and meso- and macroporous silicates [33–35], calcium and barium sulfates and carbonates [25, 30, 36], activated carbon [14, 15, 37], and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [38] are used as supports. Nickel on kieselguhr [7] and Raney nickel [39, 40] were used in early studies and patents. Sulfide catalysts are not used in polymer hydrogenation because of high reaction temperature (290–360°C). Petroleum polymeric and indene–coumarone resins [21, 41], surpassing high-molecular-mass polymers in the heat resistance, are an exception.

Calcium and barium sulfates and carbonates are used as supports owing to large pore diameter, 1.3  $\mu\text{m}$  for BaSO<sub>4</sub>; their specific surface area is as low as 4.6 m<sup>2</sup> g<sup>-1</sup> [25]. 5% Pd/BaSO<sub>4</sub> [9, 25, 30] and 5% Pd/CaCO<sub>3</sub> [41] have been studied. The almost 100% conversion in hydrogenation of double bonds is usually reached at a temperature of ~50°C and a pressure of ~50 atm [42]. In hydrogenation of aromatic rings, the temperature is elevated to 140–190°C, and the pressure, to 70–120 atm [9, 25, 30].

Because of lower conversion of aromatic rings on finely porous catalysts, palladium on coal is used more frequently for hydrogenation of double bonds in molecules of butadiene–acrylonitrile rubbers [37] and silicon-containing polymers [14, 15]. According to [14],

this catalyst exhibits high performance in hydrogenation of sterically hindered 2-trialkoxy-substituted 1,3-butadienes at 110°C and 80 atm, whereas hydrogenation on homogeneous Wilkinson's catalyst is inefficient because of steric hindrance produced by the trialkoxy group [14]. The Pd/C catalyst is used for polystyrene hydrogenation more seldom [43]; the process is performed under relatively severe conditions: 200°C and 136 atm.

One of possible solutions of the problem concerning adsorption of high-molecular-mass polymers on active sites is the use of carbon nanotubes as supports. They have large surface area without porous structure [44, 45]. In this case, more complete adsorption on a polymer molecule in one step is reached, and the developed surface simplifies the conformational transformations of the molecule, increasing the rate and the number of reaction turnovers [45]. As a result, it becomes possible to perform the hydrogenation under milder thermobaric conditions and in concentrated solutions. For example, C=C bonds in butadiene-acrylonitrile rubber are selectively hydrogenated on the Rh/nanotubes catalyst at room temperature and a pressure of 4 MPa in a solution of 40% concentration. To compare, polymer hydrogenation is usually performed in 1–20% solutions [14, 25, 26, 29]. Successful hydrogenation in a highly concentrated solution shows that there are no diffusion or conformational limitations for this catalyst. However, when using nanotubes as a support, there is a problem with separation of the catalyst from the product and contamination of the hydrogenated polymer with the catalyst.

On the whole, distribution of active sites mainly on the external surface of the catalyst in synthesis of the support is an important issue, because polymer molecules cannot penetrate into narrow and deep pores. When using a support with a developed porous structure, a large fraction of the active component appears to be inaccessible to macromolecules and thus is lost. One of solutions is the use of cellular block catalysts [46] or of macroporous silicon oxide microspheres with hydrogenating metal nanoparticles immobilized on them [47]. In such cases, the metal is distributed mainly on the external surface of the support and is accessible to macromolecules.

Much attention is paid today to preparation of silicates with the preset pore size and narrow pore-size distribution [24, 26, 27, 35, 48, 49] to fit the mean molecular mass of the polymer. Materials with the pore

diameter of 600–800 Å (up to 10 000 Å), containing no micro- and mesopores, are being developed [35, 49]. Owing to localization of active sites in macropores only, it is possible to perform the reaction in concentrated (15–25%) polymer solutions, which reduces the process cost [49].

Hydrogenation of oxygen-containing polymers such as ketone-formaldehyde [12] and indene-coumarone resins [50] stands somewhat apart. In these processes, copper-chromium catalysts are often used; they ensure complete deoxygenation of indene-coumarone resins and partial deoxygenation of ketone-formaldehyde resins.

To complete the review of heterogeneous catalysts, let us consider some distinctive patented solutions. Promotion of palladium catalysts with alkali or alkaline earth metals [51] or preliminary treatment of polymer crumb with an alkali solution [52] is suggested; it ensures higher degree of hydrogenation of C=C bonds in isoprene, butadiene, and butadiene-acrylonitrile rubbers. The cause of this effect is yet unknown. A procedure for separating the polystyrene hydrogenation product from the initial polymer by dissolution of the mixture in an aromatic solvent, followed by precipitation of the hydrogenated product with a cyclic ether (ethylene oxide, propylene oxide, etc.) has been patented [53].

#### *Catalysis in the Dispersed Phase*

Unsupported nanosized catalysts used in hydroconversion of heavy crude oils and Fischer-Tropsch synthesis [22, 23] seem to be quite suitable for hydrogenation of macromolecular compounds owing to the absence of porous structure and diffusion limitations and to wide possibilities for controlling the nanoparticle morphology and size to meet specific requirements. However, despite these advantages, "classical" metal nanoparticles are used extremely seldom. Experiments are performed more frequently with so-called colloidal catalysts, solutions of palladium compounds from which a suspension of palladium metal is gradually formed in the course of hydrogenation, with the unchanged fraction of the compound continuing to operate as a homogeneous catalyst [4]. Thus, classical homogeneous catalysts can also undergo partial reduction in the course of the reaction, transforming into heterogeneous catalysts.

Unsupported catalysts are mentioned in review as applied to hydrogenation of polymers [2] and are

described in detail in review [4]. Catalysts of this group can be subdivided into sulfide and metal catalysts. Sulfide catalysts are molybdenum or tungsten sulfides promoted with nickel or cobalt. Because sulfides are active at 280–360°C, they are used in hydrogenation of only low-molecular-mass polymers, petroleum polymeric resins, which are resistant to thermal degradation at this temperature [54–56]. For example, ex situ synthesis of nickel (cobalt)–molybdenum–tungsten catalysts from trimetallic precursors was suggested in patents [54, 55]. Such catalysts are ideally suitable for hydrogenation of petroleum polymeric resins prepared by anionic polymerization in the presence of Lewis acids. In contrast to supported catalysts, sulfide particles do not adsorb chlorine and thus do not acquire acid properties responsible for degradation of resin molecules. In [56], we demonstrated the possibility of recycling of the catalyst for hydrogenation of petroleum polymeric resins, synthesized ex situ from oil-soluble precursors.

Unsupported metal catalysts (palladium, nickel, and rhodium particles) are used more frequently than sulfide catalysts. Inorganic salts, carboxylates, and various complex compounds are used as precursors, with palladium acetate being used most frequently [57, 58]. The performance of catalysts formed in situ from various precursors in hydrogenation of butadiene–acrylonitrile rubber is compared in patent [59] (Table 1). As can be seen, the bulkier the ligand is, the higher is the degree of hydrogenation. This is associated with low solubility of inorganic palladium salts in the solvent used (acetone), with particle agglomeration in the course of reduction, and with low dispersity of the catalyst formed.

In this connection, various procedures are used for size control and stabilization of the particles formed. In particular, carboxylates with long alkyl chain (stearate, oleate) can be used instead of palladium acetate [60]. Introduction of butadiene–acrylonitrile rubber in the solution of the catalyst precursor in the course of ex situ reduction is suggested [60]. In this case, the performance of the catalyst synthesized from palladium acetate increases: The degree of hydrogenation of C=C bonds increases from 32 to 97% in butadiene–acrylonitrile rubber and from 13 to 67% in polybutadiene.

As noted in [61], palladium forms a colored complex with butadiene–acrylonitrile rubber. This complex can be isolated and used in catalysis of the polymer hydrogenation. Under equal conditions, the degree of hydrogenation of butadiene–acrylonitrile

rubber increases from 5 to 88% relative to palladium chloride. Similarly, polymers can be used in ex situ synthesis of nickel particles from a chloride solution, followed by the use of these particles in hydrogenation of butadiene–acrylonitrile rubber [62]. Along with polymers, the following complexing agents can be used: tetraalkylammonium hydroxide, phenyl dihydrogen phosphate, and dibenzylideneacetone; in so doing, the reduction is performed in situ [63]. A novel procedure for hydrogenation of butadiene–acrylonitrile rubber was suggested in patent [64]: The polymer is impregnated with a solution of a palladium compound, dried, and hydrogenated without solvent at 20–60°C. The degree of hydrogenation reaches 99% at a hydrogen pressure of 2.8 MPa and a reaction time of 15.5 h.

Preparation of metal (nano)particles in situ requires thorough choice of the solvent, taking into account the solubility of both the polymer and precursor. For example, the use of palladium acetate in chlorobenzene or chloroform is inefficient, in contrast to acetone and ethyl acetate [57]. In addition, the problem of the catalyst separation from the product and recycling should be solved. None of the above-considered studies on hydrogenation on metal catalysts pay due attention to this issue. It is also interesting to study changes in the catalyst performance in repeated use and the risk of the particle agglomeration.

Presumably, one of promising research lines in this field is revealing the possibilities of purposeful synthesis of nanoparticles of required size and determining the optimum particle size for hydrogenation of polymers of different molecular masses and structures.

### *Homogeneous Catalysis*

Homogeneous catalytic hydrogenation of unsaturated polymers is a postpolymerization process used for modifying the chemical and physical properties of the initial polymer. As a wide range of unsaturated polymers of various microstructures are available, selective reduction of C=C bonds is a potential route to a wide range of specialty polymers. By decreasing the degree of unsaturation, it is possible to optimize the physical properties of the polymer, such as tensile strength, relative elongation, and resistance to heat, light, and solvents [65].

Since the late 1970s, much attention was paid to homogeneous catalysts based on platinum metals,

especially to their use in reactions involving polymers [66]. The use of a homogeneous catalyst with a strictly defined molecular structure allows complete monitoring of the catalytic process and interpretation of the reaction mechanism making the major contribution to quantitative hydrogenation. It also furnishes information required for optimizing and controlling the reaction process.

In a homogeneous catalytic system, the substrate and catalyst occur in a single (in particular, liquid) phase. The overall procedure of the homogeneous hydrogenation of a polymer is similar to that of the heterogeneous hydrogenation. First, a polymer is dissolved in an appropriate organic solvent to obtain a homogeneous solution. For example, it is preferable to dissolve butadiene–acrylonitrile rubber in chlorobenzene, acetone, or methyl ethyl ketone, whereas butadiene–acrylonitrile rubber is better soluble in toluene or cyclohexane. After preparing the polymer solution, the catalyst (as a solid or a solution) is mixed with the polymer solution in a hydrogen atmosphere. After the hydrogenation completion, the subsequent steps include isolation of the hydrogenated polymer and separation and recycling of the catalyst; the latter is, certainly, considerably more labor-consuming than for a heterogeneous catalyst [67].

The majority of papers on polymer hydrogenation deal with selective hydrogenation of unsaturated

olefin C=C groups in butadiene–acrylonitrile rubber. The use of Wilkinson's catalyst  $\text{RhCl}(\text{PPh}_3)_3$  for their hydrogenation was patented in the mid-1970s by Bayer A. G. (now Lanxess Inc.) [68]. The initial studies have shown that  $\text{RhCl}(\text{PPh}_3)_3$  is an effective hydrogenation catalyst with excellent selectivity and can operate well in highly concentrated polymer solutions at high temperatures and pressures. Commercial processes of BNR hydrogenation using platinum group metals are optimized, as a rule, from the viewpoint of minimizing the catalyst concentration relative to the polymer. Hence, the preferential operation conditions usually include temperatures higher than  $100^\circ\text{C}$ , pressures higher than 2.7 MPa, and polymer concentrations about 2–10 wt %. It was also found that excess free  $\text{PPh}_3$  should be added to the reaction mixture to reach quantitative hydrogenation of C=C bonds in the presence of  $\text{RhCl}(\text{PPh}_3)_3$  [66].

The mechanism of the homogeneous hydrogenation of BNR on Wilkinson's catalyst is shown in Fig. 1. Despite the fact that the process is termed homogeneous, it is accompanied by the hydrogen transfer from the gas phase to the liquid phase. Pan and Rempel [69] have found that the hydrogenation is a first-order reaction with respect to  $[\text{Rh}]$ ,  $[\text{C}=\text{C}]$  in BNR, and  $[\text{H}_2]$  at a low hydrogen pressure:

$$R_{\text{H}} = \frac{k'KK'K_1[\text{H}_2][\text{Rh}][\text{C}=\text{C}]}{KK_1 + K'[\text{PPh}_3] + KK'[\text{H}_2][\text{PPh}_3] + KK'K_1[\text{H}_2] + KK_1K_5[\text{CN}] + KK_1K_2K'[\text{H}_2][\text{CN}]} \times 100\%,$$

where  $R_{\text{H}}$  is the hydrogenation rate;  $k'$ , rate constant; and  $K$ ,  $K'$ ,  $K_1$ ,  $K_2$ , and  $K_5$ , equilibrium constants.

This rate equation and this mechanism can also describe the hydrogenation of butadiene and butadiene–styrene rubber. In this case, the equilibrium constants  $K_2$  and  $K_5$  become zero.

When using polymers as substrates, higher performance of homogeneous catalysts over heterogeneous catalysts is an advantage. Low rates and low yields observed in such reactions in the presence of heterogeneous catalysts are usually attributed to hindered orientation of a long polymer chain on an immobile active site of the catalyst [70], whereas homogeneous catalysts are mobile and exhibit high activity and selectivity [67].

Despite these advantages, homogeneous catalysts are used in industry considerably more seldom than hetero-

geneous catalysts. The use of a homogeneous catalyst involves problems mainly in production of polymers of high economic value. This is associated, as a rule, with relatively high production cost of the homogeneous catalyst and with problems arising in separation of the catalyst from the final product. The catalyst loss with the product increases the production cost.

The most widely used homogeneous catalysts for polymer hydrogenation are soluble transition metal complexes. Owing to their high activity and selectivity, it is possible to selectively hydrogenate C=C bonds in the presence of other functional groups also capable of hydrogenation [71]. Today the only commercially available catalysts are probably homogeneous rhodium complexes such as Wilkinson's catalyst and palladium colloids prepared from  $\text{Pd}(\text{OAc})_2$  complexes [72].

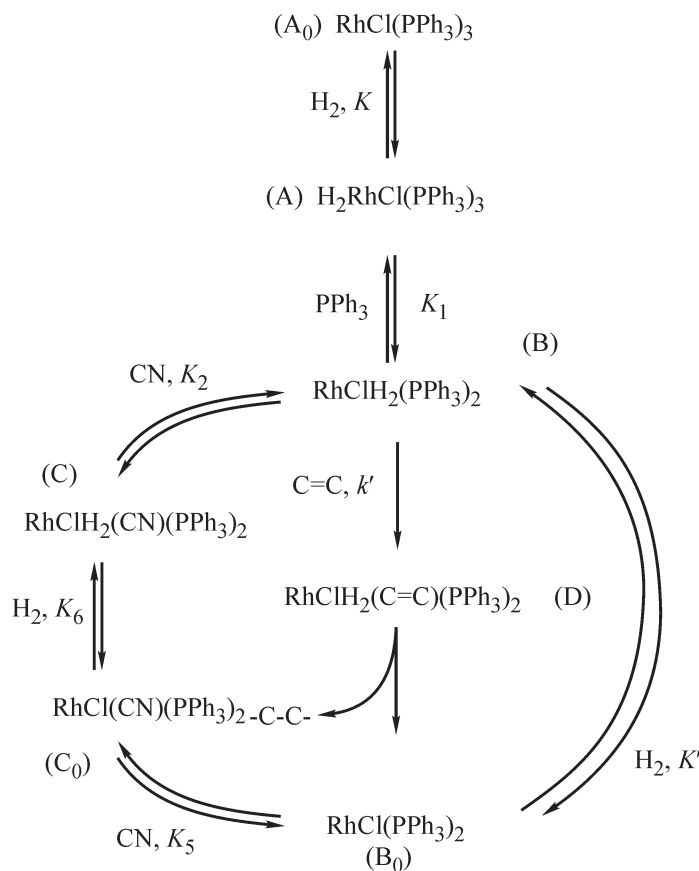


Fig. 1. Mechanism of hydrogenation of diene polymers on Wilkinson's catalyst [69].

Among the catalysts studied, the major attention was paid to rhodium-based catalysts. Wilkinson's catalyst is stable and shows excellent selectivity to olefin C=C double bonds [67, 71].

Along with the use of Rh complexes, attempts were made to use other catalysts based on transition metals in BNR hydrogenation (Table 2) [67].

Homogeneous catalysts based on ruthenium, osmium, iridium, and palladium were also studied and showed high activity in hydrogenation of diene polymers containing no other groups capable of hydrogenation. For example, the degree of hydrogenation of the styrene–isoprene–styrene triblock copolymer on  $\text{Pd}(\text{OAc})_2$  was about 90 mol % in 1 h at 60°C and the hydrogen pressure of 1.4 MPa in a chloroform–acetone mixture [79]. Hinchiranan et al. [80] studied the kinetics of hydrogenation of natural rubber on  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  catalyst. This catalyst showed high performance in hydrogenation of natural rubber dissolved in monochlorobenzene. The degree of hydrogenation was

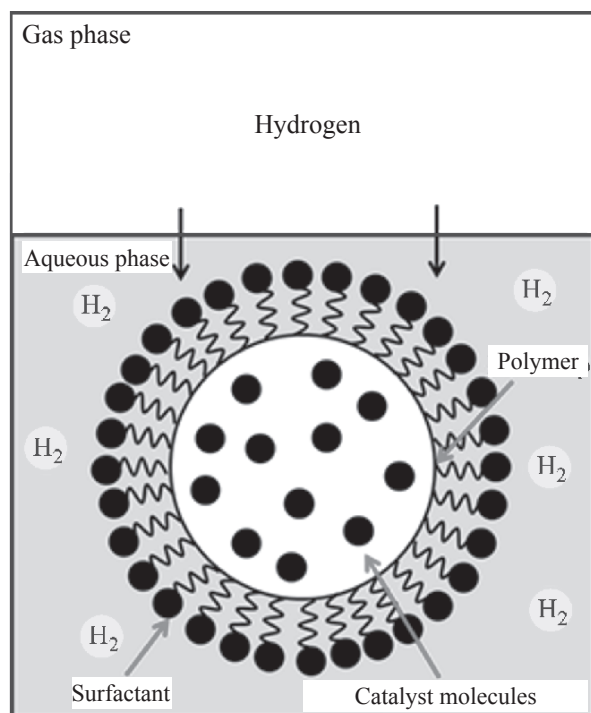
Table 1. Comparative data on the performance exhibited in hydrogenation of butadiene–acrylonitrile rubber by palladium catalysts formed from different precursors [59]. Reaction conditions: 500 ppm of Pd relative to the polymer, 50°C, 50 atm, 6 h, autoclave

Precursor	Degree of hydrogenation of C=C bonds, %
$\text{PdCl}_2$	5.3
$\text{Pd}(\text{NO}_3)_2$	6.9
$\text{PdCl}_2(\text{norbornadiene})$	45.5
$\text{PdCl}_2(\text{CH}_3\text{CN})_2$	84.9
$\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$	82.3
$[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$	71.5
Pd acetylacetonate	73.2
$\text{PdCl}_2(\text{S}(\text{CH}_3)_2)_2$	43.5

**Table 2.** Hydrogenation of butadiene–acrylonitrile rubber on catalysts based on noble metals [67]

Metal	Drawback compared to rhodium	References
Ruthenium	Degradation and cross-linking at high temperatures and pressures; C=C isomerization; formation of the inactive form, Ru–CN, in BNR hydrogenation	[2, 73, 74]
Osmium	Cross-linking in late stages of hydrogenation	[72, 75, 76]
Iridium	Low conversion, low catalytic performance	[70, 77]
Palladium	Low degree of hydrogenation	[57, 78]

more than 90% at 140°C and pressure of 2.76 MPa in 10 min. In [81], the degree of hydrogenation of *cis*-1,4-polyisoprene in mono-, di-, and trichlorobenzene and in dichloromethane in  $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$  was more than 95% in 30–40 min, and the degree of hydrogenation of natural rubber in mono- and dichlorobenzene on the same catalyst was more than 90% in 1–1.5 h at 130°C and the hydrogen pressure of 2.76 MPa. At higher hydrogen pressures, the polymer molecules underwent cross-linking. The ruthenium analog of Wilkinson's catalyst showed high performance in hydrogenation of a solution of butadiene–styrene rubber in toluene [82]. The degree of hydrogenation of the polymer reached 100% in 12 h at 100°C and the hydrogen pressure of 5.88 MPa.

**Fig. 2.** Diagram of three-phase hydrogenation of unsaturated polymer [90].

Along with studies in the field of polymer hydrogenation on platinum group metals, there are also studies on homogeneous hydrogenation on Ziegler–Natta type catalysts using nickel and cobalt chelate complexes and Group I, II, and IIIA metal alkyls. These catalysts were extensively studied until 1980. Their use is mainly limited to hydrogenation of polybutadiene [83, 84], polyisoprene [83, 85], butadiene–styrene rubber [86–88], and isoprene–styrene copolymers [89]. The hydrogenation conditions on these catalysts are relatively mild, because such systems can catalyze side processes; e.g., BSR hydrogenation can be accompanied by hydrogenation of the aromatic ring. An advantage of Ziegler–Natta type catalysts over homogeneous catalysts based on platinum metals is low cost. High selectivity of the process can be reached by properly choosing the feedstock and hydrogenation conditions.

Much attention has been paid recently to hydrogenation of latexes [90]. This is a postpolymerization process of direct hydrogenation of particles of an unsaturated polymer in a stable emulsion, preferably in an aqueous medium (Fig. 2).

The first report on hydrogenation of BNR latex was made by Weinstein [91] in 1984. Hydrogenation was performed using Wilkinson's catalyst at 70–75°C and the initial hydrogen pressure of 0.24–0.275 MPa, but the hydrogenation product was acrylonitrile–ethylethylene–tetramethylene copolymer rather than hydrogenated BNR. The modern commercial process for hydrogenation of diene (BNR, BSR, isoprene and butadiene rubbers) latexes is hydrogenation in solution. It usually starts from rubber recovery from its initial latex and its subsequent purification. Such procedure makes the process more expensive compared to direct latex hydrogenation and gives rise to environmental problems. Hydrogenation of an unsaturated polymer in latex allows the labor-consuming dissolution and



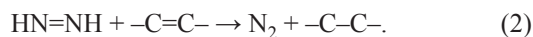
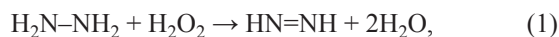
separation steps involved in solution hydrogenation to be avoided, the use of undesirable solvents to be restricted, and the amount of chemical waste to be minimized [90].

### *Hydrogenless Hydrogenation*

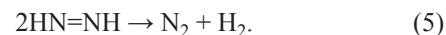
The procedures for hydrogenation of macromolecular compounds without using gaseous hydrogen include catalytic hydrogenation in the presence of hydrogen donors and noncatalytic processes of reduction with diimide. The hydrogen donors used include formic acid and formates, limonene, tetralin, cyclohexene, indoline, benzyl alcohol, etc.; the process is performed in the presence of traditional catalysts or unsupported metal particles [92, 93]. Hydrogenation of butadiene–styrene rubber in limonene on Pd/C catalyst was studied in detail [94]. The process was performed at atmospheric pressure and boiling point of limonene (176°C); aromatic rings were not hydrogenated under these conditions, and the degree of hydrogenation of double bonds remained relatively low, 70%. On the whole, such processes are rather of scientific interest, and their commercial implementation will hardly be efficient.

Noncatalytic hydrogenless hydrogenation is a cheaper process compared to catalytic hydrogenation using transition metals [95]. Hydrogenless hydrogenation of unsaturated polymers is performed most frequently using diimide generated in situ from hydrazine hydrate or *p*-toluenesulfonylhydrazide. Other arenesulfonylhydrazides [96, 97] and potassium azodicarboxylate [95, 96] are used more seldom. The degree of hydrogenation of polymers in such process can exceed 90% [95, 98–103]. The side process is the polymer cross-linking, which can be minimized by adding hydroquinone [99, 104], sodium *N,N*-dimethyldithiocarbamate [98], *p*-*tert*-butylcatechol [98], Irganox [104], and some other inhibitors [103].

The use of hydrazine hydrate as a source of diimide requires the presence of an oxidant. Hydrogen peroxide is used as an oxidant most frequently. The process occurs as follows [98, 105]:



Along with reactions (1), and (2), some other reactions can occur in the system [105, 106]:

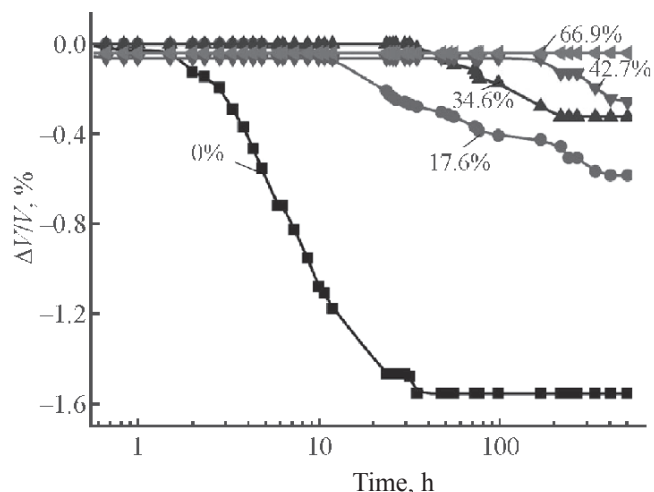


With other oxidants used instead of hydrogen peroxide, the generation of diimide from hydrazine occurs similarly [101, 104]. The following agents are used in various studies for activating and accelerating the diimide generation from hydrazine:  $\text{Cu}^{2+}$  [106, 108] and  $\text{Fe}^{3+}$  [98] ions, selenium [104, 109, 110], and boric acid [99, 102, 105, 107]. The process is performed at 30–70°C. Selective hydrogenation of double bonds is observed under these conditions.

The use of *p*-toluenesulfonylhydrazide requires heating to ensure the decomposition into diimide and *p*-toluenesulfonic acid [95]. *p*-Toluenesulfonylhydrazide was used for the first time as a source of diimide in hydrogenation of double bonds in polyvinyl chloride. Hydrogenation using *p*-toluenesulfonylhydrazide is usually performed at elevated temperatures (110–160°C) in high-boiling aromatic solvents. At these temperatures, the precursor decomposes, and double bonds are hydrogenated [2]. Noncatalytic hydrogenation using *p*-toluenesulfonylhydrazide is more applicable to diene polymers containing no other functional groups susceptible to hydrogenation. For example, hydrogenation of epoxidized natural rubber was accompanied by partial opening of epoxy rings [111], and hydrogenation of carboxylated natural and synthetic rubber was accompanied by decarboxylation to 34 and 42%, respectively [100].

### DISTINCTIVE FEATURES OF HYDROGENATED POLYMERS

Hydrogenation is one of the most efficient methods for modifying polymers, enhancing their oxidation resistance, chemical stability, and mechanical properties and reducing the gas permeability [2, 3, 112, 113]. Hydrogenation of double bonds also enhances the polymer resistance to ozone, hydrogen sulfide, acids, and petroleum products. The heat resistance is also appreciably enhanced, as demonstrated in Table 3 by the example of several polymers [2]. The only factor restricting wider use of hydrogenated polymers is high cost of their production [66]. The properties of hydrogenated macromolecular compounds will be presented in this section for each type of polymers separately.



**Fig. 3.** Variation of the volume at  $-25^{\circ}\text{C}$  for natural rubber with different degrees of hydrogenation (indicated at curves) [113].

**Natural rubber.** Hydrogenation of natural rubber, whose heat resistance is unsatisfactory, appreciably increases the degradation onset temperature (Table 3) and the activation energy of thermal degradation (from 179 to 236  $\text{kJ mol}^{-1}$ ) [114]. The degradation onset temperature increases with an increase in the degree of hydrogenation [113]. Composites containing hydrogenated and nonhydrogenated rubber have the degradation onset temperature of the nonhydrogenated rubber, because these polymers are incompatible in a blend [114].

As expected, an increase in the degree of hydrogenation leads to an increase in the ozone resistance of the rubber, expressed in the number and depth of cracks after treatment with ozone [115]. The glass transition point of rubber slightly increases with the degree of hydrogenation because of a decrease in the number of double bonds and in the flexibility of the

macromolecule [113]. The resistance of the polymer to low temperatures increases considerably. For natural rubber, this property is determined by its ability for crystallization: The material becomes brittle upon crystallization. Figure 3 shows how the rubber volume varies with time of keeping at  $-25^{\circ}\text{C}$  [113]. The decrease in the volume suggests crystallization. As can be seen, the crystallization occurs in 7 h for the nonhydrogenated rubber, in 33 h for the 34.6% hydrogenated rubber, and in 167 h for the 42.7% hydrogenated rubber. The volume of the rubber with 66.9% degree of hydrogenation does not change noticeably, suggesting no crystallization and excellent resistance to low temperatures. This fact can be attributed to disturbance of the regular structure of the rubber molecule upon partial hydrogenation, eliminating its tendency to crystallization.

**Butadiene–acrylonitrile rubber.** Hydrogenated butadiene–acrylonitrile rubber differs from the initial polymer in a number of operation characteristics: extremely high resistance to hydrocarbons, ozone, and oxygen, high wear resistance even at elevated temperatures, and ability to preserve elasticity even after the action of high temperatures [66]. These characteristics are determined by the degree of hydrogenation, content of acrylonitrile units, and molecular mass [116]. In BNR hydrogenation, pendant vinyl groups are saturated first, which is followed by saturation of  $\text{C}=\text{C}$  bonds in 1,4-units in the backbone. At 44% degree of hydrogenation, only  $\text{C}=\text{C}$  bonds in 1,4-units remain in the macromolecule [117].

The residual content of double bonds directly influences the low-temperature behavior of BNR. According to [118], the glass transition point  $T_g$  of hydrogenated BNR is higher than that of the initial BNR. According to other data [119], the dependence is nonlinear, and  $T_g$  is determined simultaneously by the

**Table 3.** Comparative characterization of the heat resistance of the initial and hydrogenated polymers [2]

Polymer	Degradation onset temperature, $^{\circ}\text{C}$	Maximal degradation temperature, $^{\circ}\text{C}$
Natural rubber	361	387
Hydrogenated natural rubber	420	449
Butadiene–styrene rubber	397	445
Hydrogenated butadiene–styrene rubber	430	473
Butadiene–acrylonitrile rubber	400	433–476
Hydrogenated butadiene–acrylonitrile rubber	445	495

degree of hydrogenation and content of acrylonitrile units. For example, at low (up to 28%) acrylonitrile content,  $T_g$  of the hydrogenated polymer is higher than that of the initial polymer. At 34–37% content of acrylonitrile units,  $T_g$  has a minimum at a certain degree of hydrogenation, with  $T_g$  of the hydrogenated polymer being higher than or equal to  $T_g$  of the initial polymer. At high acrylonitrile content,  $T_g$  slightly decreases with an increase in the degree of hydrogenation. This effect is accounted for by the loss of the chain flexibility at high acrylonitrile content, so that the dependence of  $T_g$  on the degree of hydrogenation becomes weak. At low acrylonitrile content, hydrogenation decreases the flexibility of the initially mobile chain, and  $T_g$  increases. An increase in the degree of hydrogenation leads to a decrease in the brittle point (Fig. 4) [119], which, as in the case of natural rubber, can be attributed to the loss of the ability to crystallize.

Owing to the absence of C=C double bonds, hydrogenated BNR is resistant to  $H_2S$ ,  $CO_2$ ,  $CH_4$ , hydrocarbons [2], and chloroform [120]. Table 4 shows how characteristics of BNR samples with different degrees of hydrogenation vary after the action of mineral oil at 150°C for 168 h [2]. As can be seen, the ultimate tensile strength of the hydrogenated samples

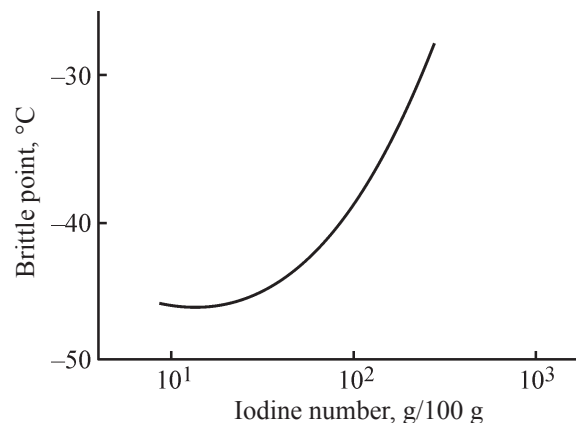


Fig. 4. Brittle point of BNR as a function of the iodine number (37% content of acrylonitrile units) [119].

only slightly changes after the action of oil. However, the hydrogenated polymers show stronger tendency to swell in oil.

The mechanical properties are slightly improved upon hydrogenation. For example, for sulfur vulcanizates of the initial and hydrogenated BNR (degree of hydrogenation 93%), the tensile strength is 20.5 and 22.3 MPa, and the elastic modulus at 100% elongation is 3.4 and 5.9 MPa, respectively [2].

Table 4. Variation of the mechanical properties of peroxide vulcanizates of butadiene–acrylonitrile rubber under the action of mineral oil [2]

Parameter	BNR	Hydrogenated BNR with indicated degree of hydrogenation, %			
		93	95	99	99.5
Before keeping in oil					
Shore A hardness	75	78	80	79	81
Elastic modulus at 100% elongation, MPa	7.6	8.3	9.2	5.9	7.6
Tensile strength, MPa	20.7	22.1	23.0	23.4	21.5
Limiting elongation, %	190	220	220	270	250
After keeping in oil					
Absolute change in Shore A hardness	–1	–9	–6	–10	–13
Absolute change in elastic modulus at 100% elongation, MPa	–	+1	0	–27	–26
Absolute change in tensile strength, MPa	–67	–1	–10	–9	–4
Limiting elongation, %	190	220	220	270	250
Volume change, %	+13	+17	+12	+19	+17

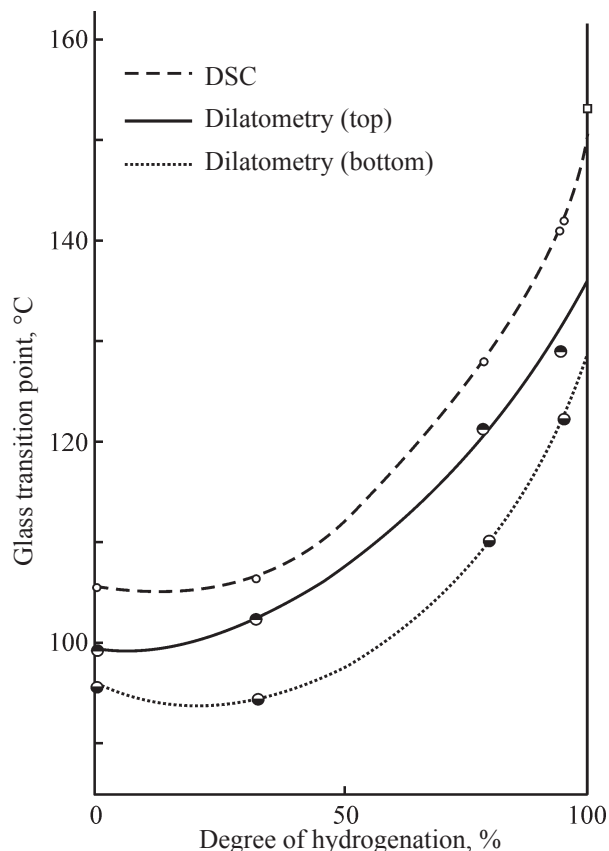


Fig. 5. Glass transition point as a function of the degree of polystyrene hydrogenation [96].

The mechanical properties of hydrogenated BNR are preserved not only under the action of petroleum products and aggressive gases, but also under the action of heat. For example, the relative elongation of hydrogenated BNR after keeping in air at elevated temperature varies to a lesser extent than for the initial rubber [121]. On the whole, the resistance to oxidation and heat is enhanced by increasing the degree of hydrogenation and the content of acrylonitrile units. The polymer properties change owing to two processes: chain degradation leading to a decrease in the molecular mass and cross-linking leading to an increase in the molecular mass. In the first case, thermal degradation is observed. This pathway is characteristic of polymers with high degree of hydrogenation, high molecular mass, and low content of acrylonitrile units. Degradation accompanied by an increase in the molecular mass is characteristic of BNR samples with high residual content of C=C bonds; in this case, the oxygen addition to double bonds and the chain cross-linking occur. For example, BNR with 85% degree of hydrogenation can be stable at 190°C, but it

250–260°C it undergoes intense cross-linking with an increase in the Mooney viscosity [116].

The hydrogenation makes BNR more compatible with other polymers: polyethylene [122] and polyvinyl chloride (PVC) [123]. It is believed that hydrogenation enhances the mobility of trans-1,4-segments, thus enhancing the interaction of BNR molecules with PVC. In contrast to nonhydrogenated BNR, which is incompatible with polyethylene, blends of hydrogenated BNR and polyethylene behave as thermoplastics, exhibit no signs of incompatibility, and have improved mechanical properties [122]. Almost all the mechanical properties of the blends are preserved even after heat treatment. The same can be noted for blends with PVC (Table 5).

**Polystyrene and styrene copolymers.** Hydrogenated polystyrene (polycyclohexylethylene, PCHE) is characterized by enhanced resistance to high temperatures, oxidants, and UV radiation and by decreased photoelasticity coefficient [124] (Table 6).

According to [125], the glass transition point of PCHE is lower than that of the initial polystyrene owing to disturbed  $\pi$ - $\pi$  interaction of the benzene rings. However, other papers [124, 126–131] report an opposite relationship:  $T_g$  of PCHE is higher than that of polystyrene and nonlinearly increases with an increase in the degree of hydrogenation. The data obtained in [125] may be affected by the use of a high-boiling solvent, decalin, for hydrogenation; it may be distilled off from the product incompletely, leading to a decrease in  $T_g$ . The glass transition point increases insignificantly up to 50% degree of hydrogenation, after which it increases sharply (Fig. 5) [126, 127].

At low degree of hydrogenation, the polymer is a styrene–vinylcyclohexane copolymer of irregular structure, and  $T_g$  is determined by the presence of polystyrene units. At high degree of hydrogenation, cyclohexane rings sterically hinder the chain motion and packing, in contrast to planar benzene rings. In the cyclohexane ring, the carbon atoms are  $sp^3$ -hybridized, and the ring itself has the chair conformation and occupies a larger volume than the phenyl substituent does. An increase in the substituent volume leads to an increase in the energy required for the chain motion [132] and to a decrease in the chain mobility, which leads to an increase in  $T_g$  [126, 128, 130]. Hahn [126] believes that the presence of a bulky substituent hinders the chain packing, leading to a decrease in the density, noted in [124, 126]. Thus, a decrease in the chain mobility due to the presence of a bulky cyclohexyl group influences the polymer proper-

**Table 5.** Variation of the mechanical properties of blends of butadiene–acrylonitrile rubber with polyethylene and polyvinyl chloride after keeping at 150°C [91]

Parameter	BNR/ polyethylene	Hydrogenated BNR/ polyethylene	BNR/PVC	Hydrogenated BNR/PVC
Before heat treatment				
Tensile strength, MPa	1.02	5.6	6.8	7.4
Limiting elongation, %	110	420	650	560
Irreversible strain, %	20	18	29	24
After keeping at 150°C for 80 h				
Tensile strength, MPa	Blend failure	4.1	7.0	7.5
Limiting elongation, %	"	280	118	200
Irreversible strain, %	"	8	20	16

**Table 6.** Physicochemical characteristics of polystyrene and polycyclohexylethylene [124]

Parameter	PCHE	Polystyrene
Glass transition point, °C	147	106
Density, g cm <sup>-3</sup>	0.947	1.060
Heat capacity at 25°C, J g <sup>-1</sup> K <sup>-1</sup>	2.0	1.2
Light permeability, %	91	91
Water absorption at 23°C in 24 h, %	0.025	0.060
Thermal expansion coefficient, μm m <sup>-1</sup> deg <sup>-1</sup>	64	69
Poisson coefficient	0.343	0.337
Bending elastic modulus at 25°C, GPa	2.8	3.1
Molecular mass of the coil	40000	13309
Photoelasticity coefficient, 10 <sup>-12</sup> , Pa <sup>-1</sup>	-200	-4700

ties more strongly than  $\pi$ - $\pi$  interactions of the phenyl substituents do [131].

On the other hand, the presence of bulky cyclohexyl substituents allows a larger number of chains to be accommodated in one coil, which is manifested in an increase in the mean molecular mass of the coil,  $M_e$ , relative to polystyrene (Table 6) [124, 130]. In other words, according to [124, 130], the presence of cyclohexyl substituents leads to denser chain packing, manifested in an increase in  $M_e$  and brittleness of the polymer and in the number of carbon atoms in the chain between interweaving sites.

According to [132], the bulky cyclohexyl substituent prevents crystallization at the degree of hydrogenation from 23 to 61%. Completely hydrogenated PCHE, however, is capable of crystallization. Hydrogenated butadiene–styrene rubbers contain higher fraction of the crystalline phase compared to nonhydrogenated rubbers owing to the presence of  $(\text{CH}_2)_{>6}$  chains [133].

The mechanical properties of both polystyrene and styrene–diene copolymers are enhanced with an increase in the degree of hydrogenation [2, 134]. For example, the tensile strength of butadiene–styrene rubber sharply increases at the degree of hydrogenation higher than

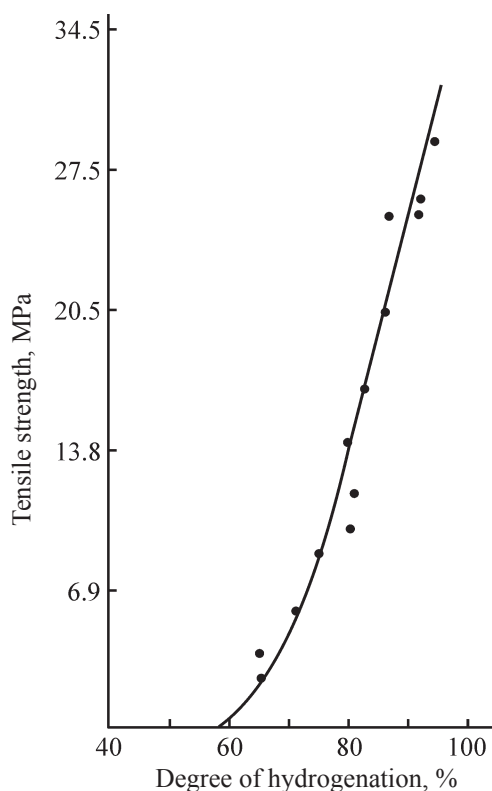


Fig. 6. Tensile strength of butadiene–styrene rubber as a function of the degree of hydrogenation [2].

60% (Fig. 6) [2]. As noted in [134], high tensile strength is preserved after the heat treatment of the hydrogenated copolymers.

#### Polybutadiene, polyisoprene, and other polymers.

The glass transition point of polybutadiene, according to [135], is independent of the degree of hydrogenation and is close to that of the initial polymer. According to other data [66],  $T_g$  of block copolymers of 1,4- and 1,2-butadiene increases upon hydrogenation. Cassano et al. [135] report that the initial and partially hydrogenated polybutadiene have close melting points; only the polymer with 100% degree of hydrogenation has higher (by approximately 3°C) melting point, which is caused by the more rigid structure of the molecule containing no double bonds. It should be noted that blends of the initial and partially hydrogenated (degree of hydrogenation 12–89%) polybutadiene are incompatible.

Hydrogenation considerably increases the tensile strength and relative elongation at break. For example, for the hydrogenated block copolymer of 1,4- and 1,2-butadiene (degree of hydrogenation 100%,  $M_n$  of 1,4-block 94 000,  $M_n$  of 1,2-block 294 000), the tensile

strength is 4.31 MPa and the relative elongation is 950%, whereas the respective values for the initial polymer are 0.83 MPa and 100% [66].

Hydrogenated polyisoprene is similar in its properties to equimolar ethylene–propylene copolymers of regular structure and has the same values of the glass transition point, density, temperature coefficient of the viscosity, and intrinsic viscosity [112]. However, hydrogenated polyisoprene is incapable of crystallization.

The other hydrogenated polymers include various styrene copolymers, including those with alkyl methacrylates [136, 137], exhibiting enhanced tensile strength, endo-dicyclopentadiene polymers with partial ring opening [138], and ketone–formaldehyde resins [10–13].

#### USE OF HYDROGENATED POLYMERS

The hydrogenated BNR and styrene–diene copolymers and PCHE are the most widely used hydrogenated polymers. Hydrogenated polybutadiene and polyisoprene are used extremely seldom, because their characteristics are similar to those of polyethylene and ethylene–propylene copolymers but the cost is high.

**Hydrogenated butadiene–acrylonitrile rubber** is used in oil-extracting industry as a material for gaskets, hoses, bearing inserts, and valve plates owing to its extremely high resistance to hydrocarbons [2, 66, 139]. The resistance to petroleum products and elevated temperatures and excellent strength properties make hydrogenated BNR a suitable material for automobile industry. It is used manufacturing pipelines for fuel system, hydrosystem, and transmission, and also gaskets and diaphragms for gear boxes, pumps, and air conditioning systems [66, 140, 141]. The oil resistance of hydrogenated BNR, polyacrylate (ACM), and ethylene–acrylate copolymer (AEM) is compared in Fig. 7 [142]. As can be seen, after keeping in oil for 1008 h the strength properties of hydrogenated BNR are preserved. The same is true for AEM but not for polyacrylate. However, hydrogenated BNR, in contrast to AEM, is characterized by high wear resistance, which makes it indispensable in production of conveyor and drive belts [2]. For example, hydrogenated BNR with 45% acrylonitrile units (ACN in Fig. 7) surpasses in the wear resistance BNR by a factor of 1.75, epichlorohydrin–ethylene oxide copolymer by a factor of 2, and polyacrylate by a factor of 2.5 [142].

Owing to enhanced resistance to ionizing radiation and steam, hydrogenated BNR is used in nuclear power engineering in fabrication of gaskets and cable insulation [2], and owing to high chemical resistance [143] it is used in military industry in fabrication of soft vessels for missile fuel [2].

Sulfur vulcanizates of hydrogenated BNR exhibit decreased levels of heat accumulation and compression set and enhanced mechanical strength [144]; peroxide vulcanizates exhibit enhanced strength and heat resistance and can be used in fabrication of cables, drive belts, and shaft covers [145]. Hydrogenated BNR can be used as composites with chloroparaffin [146] in production of adhesives and organic coatings and as composites with resorcinol-formaldehyde resin in production of adhesion promoters [147]. The following fillers are suggested for reinforcing hydrogenated rubber: carbon black [148], carbon nanotubes [149], sodium aluminosilicate [150], and silicon oxide with grafted polyvinylpyrrolidone [151].

Hydrogenated BNRs are produced under trade names Zetpol and Therban. Their grades differ in the degree of hydrogenation, content of acrylonitrile units, and Mooney viscosity. Several acrylate-modified hydrogenated BNRs and carboxylated rubber [142] are also produced under trade names Zeoforte and Therban. Adducts of partially hydrogenated BNR with chlorine and bromine have been patented [152].

*Hydrogenated polystyrene and styrene copolymers.* PCHE and hydrogenated styrene copolymers are used in automobile industry and in roof and road building owing to their weather and wear resistance [2]. Hydrogenated styrene copolymers with butadiene or isoprene are widely used as thickening additives to oils, increasing the viscosity index [5, 153–155]. As a rule, star-shaped polymers with low styrene content are synthesized. Because of specific properties of such polymers and complex dependence of their behavior in oil on the structure and degree of hydrogenation, this class of hydrogenated polymers will be considered in a separate review.

High glass transition point and decreased photoelasticity coefficient make PCHE an ideal material for fabricating optical disks, lenses, films, and optical materials as a whole [124, 156, 157]. The absence of aromatic fragments and toxicity allows the use of PCHE in food, medical, and pharmaceutical industry [2, 158]. In addition, hydrogenated butadiene-styrene rubber is

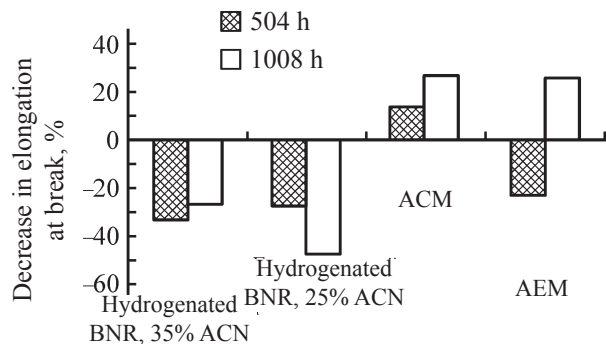


Fig. 7. Variation of the elongation at break of hydrogenated BNR, polyacrylate, and ethylene-acrylate copolymer after keeping in motor oil for 504 and 1008 h at 150°C [111].

used for producing thermoplastic compounds containing polypropylene, plasticizers, and stabilizers [159].

## CONCLUSIONS

To conclude, let us mention the commercial production problems and research prospects in the field of the polymer hydrogenation. High production cost of hydrogenated polymers restricts their wide use, despite excellent operation characteristics. This problem can be solved by finding effective catalysts and preparing macroporous supports with preset characteristics; this requires scientifically substantiated approach to choosing the pore size based on the size of polymer coils in a specific system (solvent, concentration, temperature, mean molecular mass of the polymer). Block and crust catalysts show promise, but up to now they virtually were not considered as applied to hydrogenation of macromolecular compounds. Unsupported nanosized catalysts are certainly of interest for the reasons discussed in the corresponding section. However, their use requires research work, in particular, the development of procedures for purposeful preparation of particles of optimum size and the very determination of the optimum particle size for hydrogenation of definite polymers, and also the development of procedures for separating the catalyst from the products.

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## CONFLICT OF INTEREST

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