




Review

Synthesis of 1,3-Butadiene and Its 2-Substituted Monomers for Synthetic Rubbers

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Received: 17 November 2018; Accepted: 14 January 2019; Published: 17 January 2019



Abstract: Synthetic rubbers fabricated from 1,3-butadiene (BD) and its substituted monomers have been extensively used in tires, toughened plastics, and many other products owing to the easy polymerization/copolymerization of these monomers and the high stability of the resulting material in manufacturing operations and large-scale productions. The need for synthetic rubbers with increased environmental friendliness or endurance in harsh environments has motivated remarkable progress in the synthesis of BD and its substituted monomers in recent years. We review these developments with an emphasis on the reactive routes, the products, and the synthetic strategies with a scaling potential. We present reagents that are primarily from bio-derivatives, including ethanol, C4 alcohols, unsaturated alcohols, and tetrahydrofuran; the major products of BD and isoprene; and the by-products, activities, and selectivity of the reaction. Different catalyst systems are also compared. Further, substituted monomers with rigid, polar, or sterically repulsive groups, the purpose of which is to enhance thermal, mechanical, and interface properties, are also exhaustively reviewed. The synthetic strategies using BD and its substituted monomers have great potential to satisfy the increasing demand for better-performing synthetic rubbers at the laboratory scale; the laboratory-scale results are promising, but a big gap still exists between current progress and large scalability.

Keywords: Synthetic rubber; 1,3-butadiene synthesis; biomass-derived feedstock; sustainability; functional substituents

1. Introduction

“Rubber” was coined by a chemist named Joseph Priestley in 1770. It has since come to be regarded as the “wheel” of civilization. Today, the term “rubber” is related to any material characterized by properties similar to those of natural rubber (NR). Attributed to the well-known importance of rubber since World War II, much effort has gone into producing rubbers by various synthetic routes [1]. In 2017, around 15.05 billion kilograms of synthetic rubbers were produced worldwide. The most prevalent synthetic rubber is styrene-butadiene rubber (SBR) which is derived from a copolymer of 1,3-butadiene (BD) and styrene. SBR has good aging stability and abrasion resistance [2], and it occupies about half of the market for car tires. Also widely used in tires is butadiene rubber (BR); it is made solely from the BD monomer and shows excellent wear resistance, good cold resistance, lower

heat generation, and dynamic performance. Unfortunately, BR still falls short of meeting the goal of producing rubbery materials that are more environmentally friendly or robust to harsh environments. For example, BR needs to be blended with SBR and/or NR when it is used for sidewall and tread. A lot of effort has been made to clarify the nature of BR and its blends (such as with SBR and NR), and significant progress has been achieved in the regulation of the structure and performance of the polymer [3–5].

When used in tires, the elastic properties of synthetic rubbers made from 1,3-dienes play a primary role and are enormously affected by the microstructures of the repeating units, especially the presence or absence of a side substituent [6]. For example, *cis*-1,4-polybutadiene shows flexibility and excellent strong deformation tolerance [7,8] due to its low glass transition temperature (T_g) of $-94\text{ }^{\circ}\text{C}$, which is much lower than that of the *cis*-1,4-polyisoprene with a $-\text{CH}_3$ group at 2-C (from -64 to $-70\text{ }^{\circ}\text{C}$) [9]. The latter, known as isoprene rubber (IR, the major component of NR), has excellent overall rubbery properties and is widely used as a synthetic substitute for NR without blending with other polymers. Therefore, IR can be used for carcass and off-the-road tires without blending with other rubbery materials. It can be easily concluded that the side substituent of 1,3-butadienes plays a crucial role in tuning the properties of the resulting materials.

However, serious problems are encountered when these polydienes are used for the production of mechanical engineering goods, such as heavy-lorry tires and aircraft tires, due to their inadequate mechanical properties (e.g., tensile strength, elongation at break, and tear resistance) [10]. Therefore, substituted butadienes are used to form polydienes with some BD derivatives, such as 2-phenylbutadiene, making it likely that a solution to these problems will be found. To this end, a functionalized 1,3-diene containing a rigid group is necessary.

On the other hand, it is well-known that tires are made by blending synthetic rubbers with inorganic fillers, such as carbon black and silica. Unfortunately, polydienes containing solely carbon and hydrogen always exhibit poor surface properties and low adhesive properties. Therefore, in the manufacturing of tires, fillers such as hydrophilic silica are completely incompatible with synthetic rubbers, as the resulting tires have poor tear resistance, abrasion resistance, and static toughness properties [11]. To solve this problem, considerable attention has been paid to the synthesis of polar-functionalized dienes because it is very difficult to modify inorganic fillers [9]. The incorporation of these kinds of monomers into copolymers and/or homopolymers can significantly improve the existing properties of synthetic rubbers. For example, nitrile butadiene rubber (NBR) can enhance the wear resistance of tires. Additionally, NBR is also widely used for seals, hoses, and gloves. In this respect, the polar-functionalized 1,3-diene attracts a lot of attention.

Accordingly, considering the entropy-elasticity of synthetic rubbers, various side substituents in 1,3-butadienes affect the properties of the resulting materials. To attain rubbers with tunable properties for meeting different requirements, introducing designed substituents into 1,3-butadiene is a promising strategy; it is also a great challenge, but this makes the success all the more rewarding. Functionalized monomers are also used to enhance the properties of synthetic rubbers, either by monopolymerization or copolymerization. In the present review, we highlight the following: (1) the production of BD and IP, which are in large demand in industry; (2) the synthesis of 2-substituted 1,3-butadienes with rigid groups, such as adamantly, phenyl, and its derivatives, which can be used to enhance the thermal and mechanical properties of the synthetic rubbers; and (3) the synthesis of polar-functionalized 1,3-butadienes containing O, Si, and N atoms and their unique properties for special applications. BD and IP are the basic monomers of the synthetic rubbers consumed widely in the automotive industry. Both BD and IP are mainly supplied by ethylene plants as by-products of naphtha cracking; taking sustainability into account, the alternative routes are urgently required [12]. The synthetic processes of substituted 1,3-butadienes always suffer from complicated operations under rigorous conditions.

2. Synthesis of 1,3-butadiene

At present, more than 95% of the world's total BD is produced from either naphtha cracking or *n*-butane dehydrogenation [13,14]. Unfortunately, these routes require expensive extractive distillation with a low selectivity (for BD) of around 4–5%. Besides that, the shale gas revolution has led to a decrease in the production of naphtha-based ethylene, which could reduce the production of BD too [15,16]. Additionally, the global supply of BD faces trouble due to the variation in chemical feedstock and the unstable price of petrochemicals. In Japan, 3 out of 15 ethylene production plants have been shut down in the 3 years before June 2016. [17] Therefore, the industry urgently calls for the development of an alternative process to produce BD without depending on petroleum.

The first production of BD from ethanol, carried out by Ipatiev in Russia in 1903, had a very low yield of 1.5% [18], and great improvements were achieved by Lebedev's group using an undisclosed composition [19]. A high yield and a BD selectivity of up to 70% under atmospheric pressure at 350 °C were reported. Interessen-Gemeinschaft Farbenindustrie AG (IG Farben) reported that magnesia catalysts promoted by Cr or Co exhibited a BD yield of 60% [20]. Subsequently, the ethanol-to-BD route was abandoned in the US and most European countries as this technology was deemed poorly competitive compared with the production of BD from petrochemical sources [21]. Currently, a return to the old ethanol-to-BD production route is gaining renewed interest because of its remarkable capacity for producing bio-ethanol and potential environmental benefits [22]. BD formation from ethanol has been studied intensively, and several possible BD formation proposals have been debated [19,23–35]. A reaction network proposed by Quattlebaum et al. is presented in Figure 1 [30]. Obviously, BD formation involves dehydrogenation, aldol condensation, hydrogenation, and a dehydration reaction, which implies that various active sites such as basic, acidic, and metallic species are required for an efficient catalyst in this reaction. Unfortunately, it seems very difficult to develop these multifunctional catalysts. Benefiting from an understanding of the reaction pathway, a more efficient two-step process employing acetaldehyde/ethanol as feedstock was developed (Figure 2), but there is still a lot of work to do to realize a BD production process with a yield higher than 90%. Although extensive studies have been performed over the past 3 years [36–47] (Table 1), as well as several published reviews [17,48–53], the development of efficient processes and robust catalysts still remains a challenge and issues related to carbon efficiency, catalyst cost, toxicity, feedstock tolerance and backend optimization need further investigation [49].

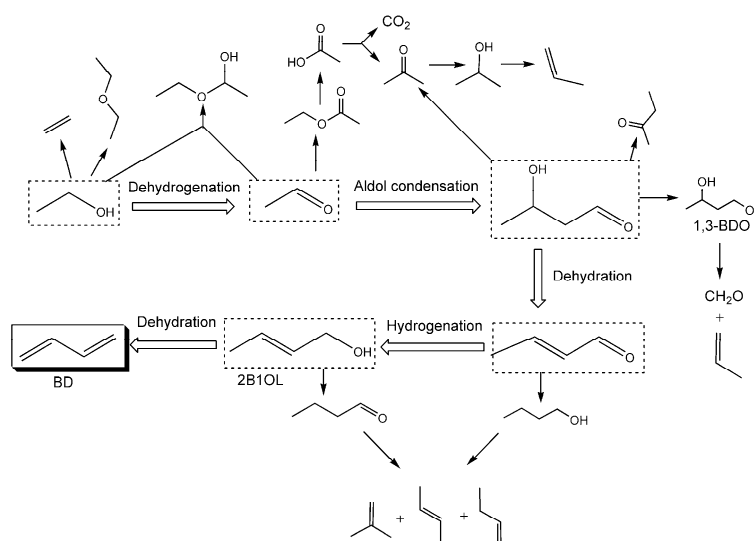


Figure 1. The general reaction mechanism and major by-products of 1,3-butadiene (BD) production from ethanol [19,23–35].

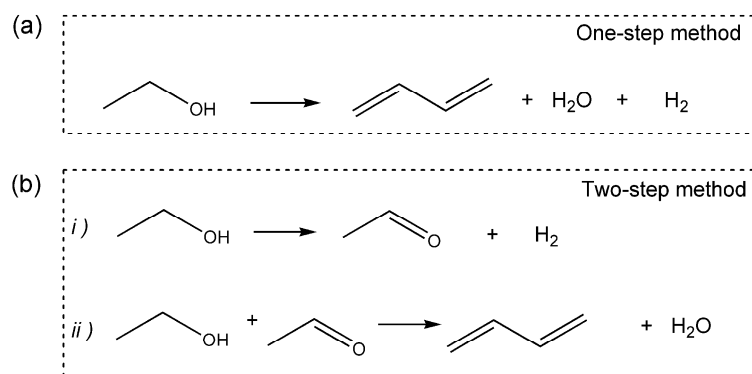


Figure 2. Synthesis of BD from ethanol. Route (a) was proposed by Ipatiev et al. [18]; Route (b) was proposed by Ostromyslensky et al. [54].

Table 1. Synthesis of BD from ethanol over various catalyst systems recently.

Catalyst	Reaction Temperature °C	Conversion%	BD Selectivity %	Ref.	BD Formation rate/mmol (g _{cat} .h) ^{−1}
ZnO–MgO/H–β280	350	43.6	63.4	[36]	0.92
NaZn ₁ Zr ₁₀ O ₂ –H	350	54.4	28	[37]	9.07
Cu/MCF–Zr/MCF	235, 400	96	37	[38]	25.92
MgO–SiO ₂ –500 ^a	500	Total 29.7	80.7	[39]	0.96
Talc/Zn	400	48.4	61.0	[40]	8.53
MgO–SiO ₂ (65:35)	450	95	77	[41]	25
3%Au/MgO–SiO ₂	300	>45	~60	[42]	2.4
Ag/Zr(3.3)BEA(38)	320	15	~60	[43]	10.3
Cu/SiO ₂ MgO/H–β280	100, 300	-	33% yield	[44]	-
Ta ₃ O ₅ SiBEA–EtOH/AA=3.2	350	58.9	73.1	[45]	-
2%ZrO ₂ /NanoSiO ₂ –500 ^a	320	58.52	93.18	[46]	-
5 % Ag/MgO–SiO ₂	275	>50	>28 yield	[47]	-
2.5% Cu–2.5%wt Ag/MgO–SiO ₂	300	60	>40 yield	[47]	-

^a Acetaldehyde was co-fed with ethanol.

Next to ethanol, alternative bio-derived C4 alcohols, such as 1,3-butanediol (1,3-BDO), 2,3-butanediol (2,3-BDO), and 1,4-butanediol (1,4-BDO), are regarded as promising feedstocks to produce BD, and their use in BD synthesis has been demonstrated (Figure 3). Makshina et al. [49] summarized this part based on many research efforts as well as reviews. They have mainly concentrated on the dehydration and deoxydehydration of these C4 alcohols to BD from the aspects of mechanistic and catalytic chemistry. Very recently, Jing et al. [55] studied the dehydration of 1,3-BDO to BD over aluminosilicates. The best result was achieved over H-ZSM-5 (silica/alumina = 260) with a BD yield of 60% at 300 °C. They pointed out that the good catalytic performance of the catalysts is a result of the presence of Brønsted acid sites with weak and medium strength. Accompanied by the unavoidable formation of carbon deposits, the conversion decreases from 100% to 80% after a 102 h run. Subsequently, Al-doped SBA-15 catalysts were applied for this reaction [56]. The highest BD yield, 59%, was achieved over Al-SBA-15 (silica/alumina = 76), with stable activity in long-term runs. Notably, the operation is performed at a relatively low temperature (200 °C).

Zeng et al. [57] studied the direct conversion of 2,3-BDO to BD over alumina catalysts with a wide range of temperatures from 240 to 450 °C. They clarified that 3-buten-2-ol (3B2OL) is a key intermediate in the dehydration of 2,3-BDO to BD by DFT, and 3B2OL can be easily converted to methyl ethyl ketone (MVK) rather than BD in the presence of sodium-modified alumina catalysts because of the natural basicity of the catalysts. The experimental results suggest that a higher selectivity to BD is obtained under a higher reaction temperature. Fang et al. [58] conducted the dehydration of 1,3-BDO to BD over a series of Ce@MOR catalysts with a flower-like morphology at 350 °C. Ce@MOR with Si/Ce at an atomic ratio of 50 presents a high 1,3-BDO conversion of 100% but a poor selectivity of 46% to BD. The high activity of Ce@MOR is attributed to the high density of Brønsted acid sites with medium

strength. Nguyena et al. [59] reported the dehydration of 2,3-BDO to BD over a GdPO_4 catalyst which resulted in the complete conversion of 2,3-BDO and a selectivity of 58% to BD at 300 °C. Both the fresh and regenerated GdPO_4 displayed relatively stable catalytic activity in a 50 h run. Kim et al. [60] carried out the direct dehydration of 2,3-BDO over silica-supported sodium phosphates catalysts at 400 °C. These findings show that the conversion of 2,3-BDO can be easily tuned up to 100%, while the selectivity to BD never exceeds 70%. All of these studies confirm that Brønsted acid sites with weak and medium strength are a key factor in the conversion of butanediols (BDOs) to BD. A great improvement was observed by Tsukamoto [61], who investigated the dehydration of 2,3-BDO to BD over SiO_2 -supported CsH_2PO_4 catalysts at 350 °C. The highest conversion of 2,3-BDO (>99.9%) and an excellent selectivity to BD (91.9%) were obtained over 10% CsH_2PO_4 , with a slight decrease over an 8 h run. This impressive catalytic activity is ascribed to a combination of the proper acid–base sites of Cs phosphate and the large ionic radius of Cs^+ , which is significantly different from Na^+ [57].

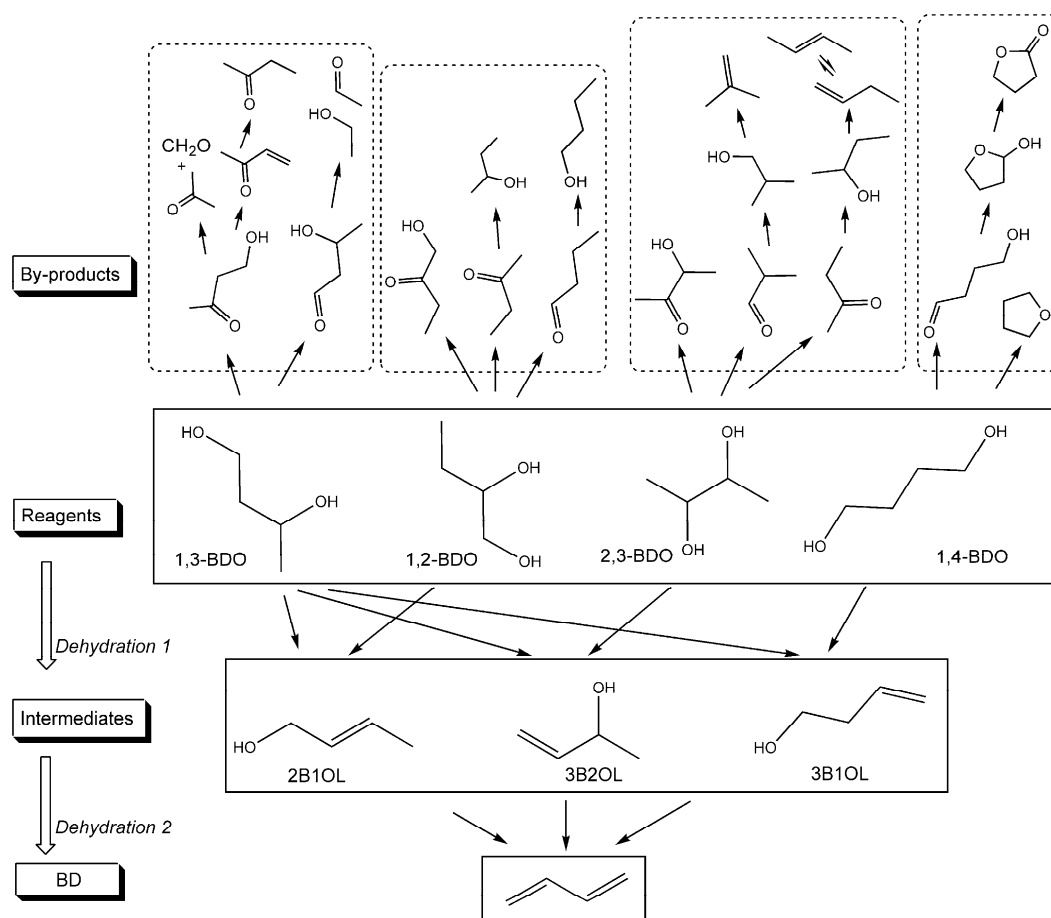


Figure 3. Synthesis of BD from butanediols (BDOs) or C4 unsaturated alcohols (UOLs) [17,62–65]. Evolution from reagents and intermediates to the target BD is labeled by arrows, and the by-products are produced during Dehydration 1.

However, the direct dehydration of C4 alcohols into BD always needs a high reaction temperature. As BD can be readily obtained via the dehydration of unsaturated C4 alcohols (UOLs) over solid acid catalysts, a novel path way to produce BD from C4 alcohols via the dehydration of C4 alcohols to their corresponding UOLs was developed, and it is performed at a relatively low temperature. Sato's group has done a lot of work in this field. Duan et al. have reviewed the dehydration of BDOs to UOLs in connection with their further dehydration to BD [17].

Not long ago, Duan et al. [62] investigated the dehydration of 2,3-BDO to 3B2OL over modified monoclinic ZrO_2 catalysts, suggesting that BaO/ZrO_2 , SrO/ZrO_2 , and CaO/ZrO_2 have good catalytic capacities. The optimized data were observed over $\text{BaO}-0.0452-800$ with a 2,3-BDO conversion of 72.4% and a 3B2OL selectivity of 74.4% during the early stage of 5 h at 350 °C. Unfortunately, a decrease in catalytic activity occurred over a long-term operation of 25 h. This is due to the formation of Perovskite compounds, such as BaZrO_3 , which are inactive for the reaction. The modified monoclinic ZrO_2 also presents high catalytic activity for the dehydration of 1,4-BDO to 3-buten-1-ol (3B1OL), especially $7-\text{CaO}+2-\text{ZrO}_2/m-\text{ZrO}_2-800$, which produces an excellent 1,4-BDO conversion of 95.2% and a high 3B1OL selectivity of 89.3% at 350 °C [63]. Then, the dehydration of UOLs to BD was conducted by Sun et al. [64] over solid acid catalysts, like $\text{SiO}_2-\text{Al}_2\text{O}_3$, Al_2O_3 , TiO_2 , and ZrO_2 , and basic rare earth metal oxides, including Yb_2O_3 and CeO_2 . This suggests that acid catalysts have a higher activity for the dehydration of 2B1OL and 3B2OL than the rare earth metal oxides. The $10\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst shows the highest 2-buten-1-ol (2B1OL) conversion (92.5%) and selectivity (75.0%) at 260 °C, but there is a rapid deactivation. Modified $10\text{SiO}_2/\text{Al}_2\text{O}_3$ with Ag can enhance the catalytic activity and inhibit the formation of carbon deposits. The best result of the dehydration of 2B1OL was achieved over $5\text{Ag}-\text{SiO}_2/\text{Al}_2\text{O}_3$, displaying a BD selectivity of 94.6% at a conversion of 99.1% at 260 °C. Also, $5\text{Ag}-\text{SiO}_2/\text{Al}_2\text{O}_3$ efficiently inhibits catalytic deactivation, with a slight decrease in the 2B1OL conversion (from 99.4% to 96.2%) and BD selectivity (from 95.0% to 87.1%) after 10 h. In contrast, the rare earth metal oxides, such as CeO_2 , show poor activity for the dehydration of 2B1OL and 3B2OL to BD, but they have a remarkable activity in the dehydration of 3B1OL to BD, which is attributed to the weak basicity and the redox nature of CeO_2 via $\text{Ce}^{4+}-\text{Ce}^{3+}$. The synthesis of BD from 3B1OL over the acid catalysts shows a much lower BD yield resulting from the C–C cleavage of 3B1OL to propylene. Thus, it is concluded that the dehydration mechanism of 3B1OL to BD is quite different from the dehydration of 2B1OL and 3B2OL.

Therefore, Wang et al. [65] studied the production of BD by the dehydration of 3B1OL and 1,4-butanediol over rare earth oxides, such as Lu_2O_3 and Yb_2O_3 . The optimal result of the dehydration of 3B1OL was obtained with a high conversion of 99.6% and a good BD selectivity of 96.7% over the Yb_2O_3 catalyst at 340 °C. Accordingly, the direct dehydration of 1,4-BDO to BD over Yb_2O_3 also exhibited excellent a catalytic performance with a yield of 96.6% at 360 °C. Thus, producing BD from bio-derived C4 alcohols and especially unsaturated C4 alcohols via the dehydration process is a promising route, although a large amount of work still needs to be done, especially for improving catalyst life for industry usage.

Tetrahydrofuran (THF) can also easily generate 1,4-BDO, which comes from five-carbon sugars such as xylose or furfural [66–69]. Therefore, Abdelrahman et al. [70] developed a novel way to synthesize BD via the catalytic ring-opening dehydration of THF, which is conducted in the presence of a solid acid catalyst with a high selectivity of 85–99% to BD at a high THF conversion of 89% (Figure 4). These encouraging data were obtained at 400 °C with a space velocity of 0.2 s^{-1} . Unfortunately, the conversion of THF significantly decreases to 8.9% with a turning space velocity of up to 9.7 s^{-1} . Therefore, a large change in this route must be implemented to improve the BD formation capacity.

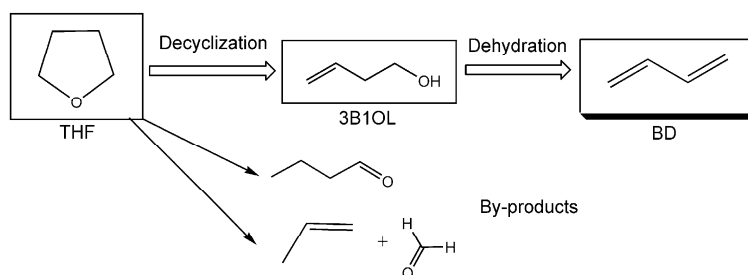


Figure 4. Synthesis of BD from THF through the intermediate 3-buten-1-ol (3B1OL), and the by-products in the decyclization of THF [70].

3. Synthesis of Isoprene

Isoprene (IP), also called 2-methyl-1,3-butadiene, is well-known as an irreplaceable monomer of synthetic natural rubber. It is a colorless liquid with a characteristic odor, and it is highly significant for producing stereoregular polyisoprene because of the ability to purposefully manipulate its properties. The huge demand for this kind of material inspires the rapid development of the synthesis of isoprene (Figure 5). The main methods used to produce isoprene in the industry have been reported elsewhere [71]. In this review, the focus is on a promising route to produce isoprene using isobutene and formaldehyde as starting materials via one step; this has attracted great interest both in the industry and in academia. This process is conducted in the presence of solid acid catalysts, such as zeolites, silver, oxide catalysts, phosphates, and heteropolyacid catalysts. Moreover, the recent development of the isoprene synthesis using another method is also presented.

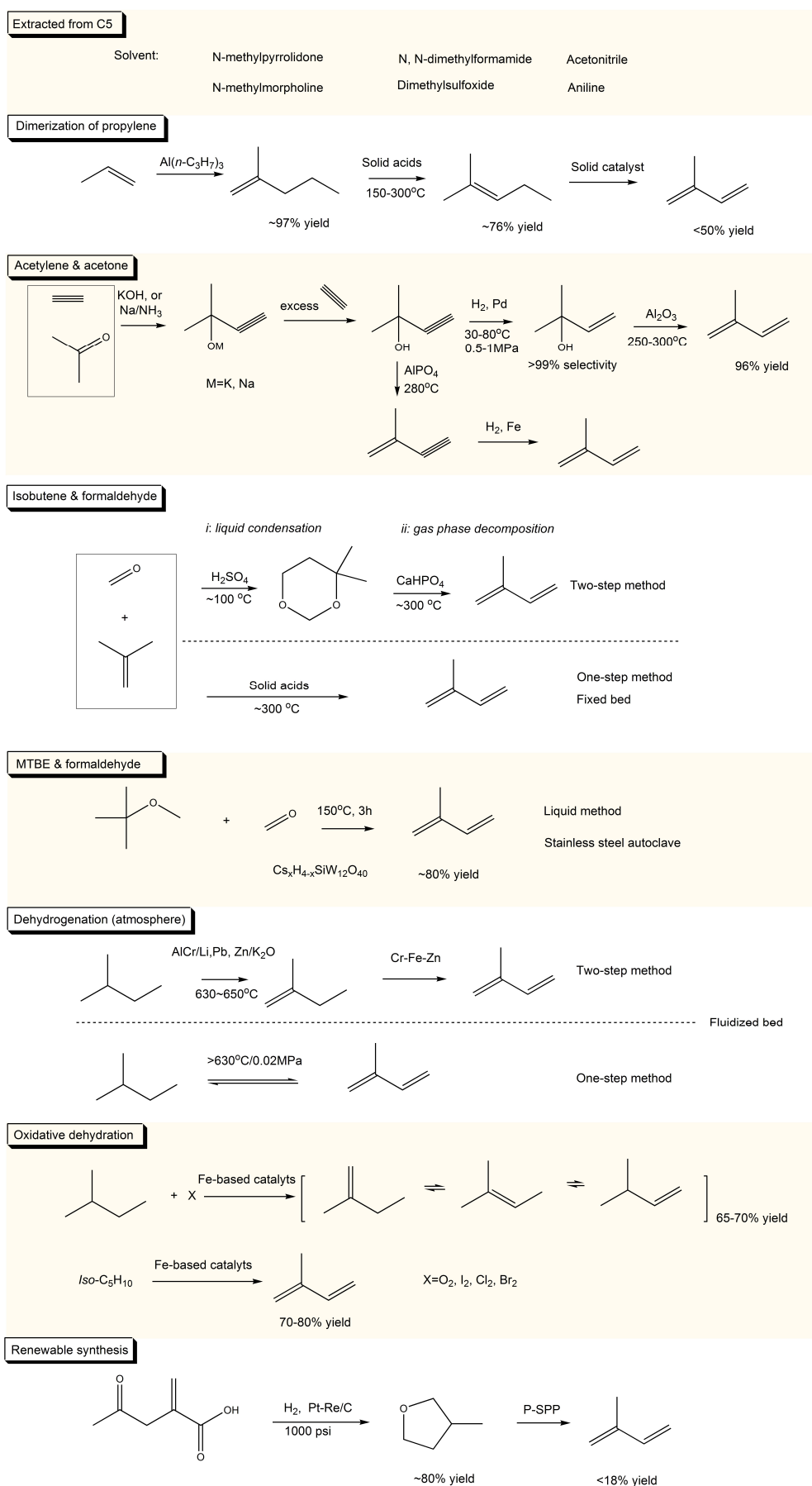


Figure 5. Overview of isoprene (IP) production routes [71–74].

Dumitriu et al. studied the reaction over zeolite catalysts [75,76]. The strength of the acid sites is suggested to play a crucial role in isoprene synthesis. The weak Brønsted acid sites on zeolites are proved to be the most efficient sites. In this respect, the highest selectivity, 99–100%, was obtained over borolites and ferrisilicates. Nonetheless, these results were obtained in a pulse catalytic reactor, which cannot be compared with those obtained in continuous flow systems.

Ag–Sb catalysts have been employed as catalysts in bed reactors and resulted in good activity, with a conversion of around 81% (for formaldehyde) and selectivity of about 70% (for isoprene). However, the activity of Ag–Sb catalysts decreases quickly and presents poor stability [77]. $\text{CuSO}_4/\text{SiO}_2$ catalysts were developed which show a formaldehyde conversion of about 63% and selectivity of about 65% to isoprene. It has been suggested that doping $\text{CuSO}_4/\text{SiO}_2$ with basic oxides to decrease the acidity can greatly improve their activity. A formaldehyde conversion of 87% and selectivity of about 65% to isoprene were obtained over $\text{CuSO}_4/\text{SiO}_2$ doped with MgO. However, the short lifetime of the $\text{CuSO}_4/\text{SiO}_2$ catalysts impedes their application in the industry, and this deficiency can be attributed to the decreasing number of acid sites resulting from the rapid formation of carbon deposits and the destruction of the CuSO_4 structure [78,79].

Krzywicki et al. [80] first reported the reaction of formaldehyde and isobutene over $\text{Al}_2\text{O}_3\text{--H}_3\text{PO}_4$ catalysts. A high H_3PO_4 content favors isoprene production owing to the increased number of acid sites. However, the phosphate catalysts still displayed low activity, with an isoprene yield of 22%. Ai et al. [81] tried to use the oxides of transition metals to improve the activity of the phosphate catalysts. MoO_3 -, WO_3 -, and V_2O_5 -based phosphate catalysts were employed for this reaction, using tert-butyl alcohol as a raw material instead of isobutene. $\text{V}_2\text{O}_5\text{--P}_2\text{O}_5$ ($\text{P}/\text{V} = 1.06$) exhibited outstanding activity, with an isoprene yield of about 60%. The author pointed out that the basic sites also play a certain role in the synthesis of isoprene. Although the phosphate catalysts show a rather excellent activity in both conversion and selectivity, they are characterized by rapid deactivation due to the formation of large carbon deposits.

Therefore, catalysts with longer lifetimes and an understanding of the influence of carbon deposition are urgently needed. Recently, Sushkevich et al. [82] conducted the condensation of formaldehyde with isobutene over a $\text{Nb}_2\text{O}_5\text{--P}_2\text{O}_5$ catalyst. This catalyst is characterized by a much longer lifetime and stable formaldehyde conversion, producing a steady isoprene yield of 57% within more than 30 h of stream. $\text{Nb}_2\text{O}_5\text{--P}_2\text{O}_5$ shows high resistance to deactivation, which is ascribed to the in situ restoration of Brønsted acid sites in the presence of water during the reaction. Moreover, spent $\text{Nb}_2\text{O}_5\text{--P}_2\text{O}_5$ can be completely regenerated by calcination at 500 °C in an air flow. It was verified that Lewis acid sites are responsible for the side reaction, which led to a low selectivity of 62.6%. Therefore, supported Keggin-type heteropolyacids catalysts with weak Brønsted sites are being developed [83,84]. Most importantly, Ivanova et al. clarified that unsaturated branched carbonaceous species in carbon deposits can generate active sites for the condensation of formaldehyde with isobutene to produce isoprene [85]. To further identify the effect of carbon deposition on the synthesis of isoprene, our group conducted the reaction over $\text{MoO}_3\text{--P}_2\text{O}_5$ [86]. 4,4-Dimethyldioxane-1,3 (DMD) has been demonstrated to be an important intermediate which can readily form on acid sites over a catalyst and further be converted into isoprene in the presence of carbonaceous species. In this regard, the formation of carbon deposits can give rise to a synergetic effect between acid species and carbonaceous species for isoprene synthesis. Slight carbon deposition is able to shorten the induction period of the reaction, while a large carbon deposition leads to catalyst deactivation because it attaches to Brønsted acid sites. For the above reasons, a simple way to restore the reactivity of deactivated phosphate catalysts was developed with the assistance of the carbon deposition [87].

Moreover, additional studies on the synthesis of isoprene by alternative routes have been reported. Songsiri et al. [72,73] synthesized isoprene using heteropolyacids as catalysts in a liquid-phase system under moderate conditions in which carbon deposits can be inhibited. Methyl tertiary-butyl ether (MTBE) was used as the source of isobutene. MTBE is more available because its use as an additive in gasoline has been prohibited in developed countries, such as the United States, Japan, and Western

Europe. High formaldehyde conversion (>95.8%) and isoprene yield (68.3–77.5%) were achieved over a Cs-exchanged silicotungstic acid catalyst. Unfortunately, it is still a challenge to completely separate the catalysts from the reaction system, and a large amount of organic solvent is employed in this process, which could result in environmental problems.

Considering environmental concerns and sustained availability, the biosynthesis of isoprene was developed based on metabolic engineering. However, the necessary productivity has not been achieved with microbes [88]. It was necessary to develop an alternative method for the sustainable production of isoprene at a large scale. Therefore, it is a promising and competitive route to convert biomass-derived feedstocks into isoprene via chemical processes. Itaconic acid from glucose [89] was employed as raw material by Abdelrahman [74]. Firstly, itaconic acid was converted into 3-methyl-tetrahydrofuran (3-MTHF) with a yield of about 80% in a liquid phase using Pd-Re/C as a catalyst. Then the dehydration of 3-MTHF was performed in a gas phase over a P-SPP (self-pillared pentasil) catalyst with an isoprene selectivity of 70% at a 20–25% conversion. For this process, much work is needed to improve the yield of isoprene, to understand the catalytic pathway, and to develop a more efficient catalysts. Extensive research on IP synthesis is urgently required, and the exploration of novel platform chemicals faces challenges, but success would be greatly rewarding.

1,3-Pentadiene (piperylene) has similar properties to isoprene and is a large-scale by-product accompanying the production of isoprene. It is widely used in the production of sticky tapes, adhesives, and plastics. In Russia, 1,3-pentadiene is also used to produce liquid rubber, which is intensively used in paint and varnish industry [90–92]. Moreover, many studies have focused on the potential application of poly(1,3-pentadiene) in the domain of elastomers. All of these factors inspire wide interest to study the production of 1,3-pentadiene [93–95]. From the view of sustainable development, many efforts have been made to develop alternative technologies for producing 1,3-pentadiene based on biomass-derived feedstocks [96–99]. Recently, Sun et al. [100] developed a novel two-step synthetic approach using xylitol as a resource (Figure 6). Xylitol is industrially produced by extracting hardwoods or corncobs. In the first step, the deoxydehydration (DODH) of xylitol was conducted at 235 °C in the presence of formic acid to give 2,4-pentadien-1-ol, 1-formate (2E), with an optimized yield of 62.9%, followed by deoxygenation to obtain 1,3-pentadiene over a Pd/C catalyst at 100 °C. The total yield of 1,3-pentadiene reached 51.8%. Kumbhalkar et al. [101] employed 2-methyltetrahydrofuran (2-MTHF) which can be easily obtained from biomass-derived intermediates (levulinic acid and furfural, etc.), as the starting material to produce 1,3-pentadiene in a continuous system. This reaction is conducted at 350 °C, and the catalyst undergoes deactivation from the formation of carbon deposits in the presence of dienes. Therefore, a decrease in the conversion of 2-MTHF (from 100% to 77%) and yield of 1,3-pentadiene (from 67.8% to 51.8%) was observed over a period of 58 h.

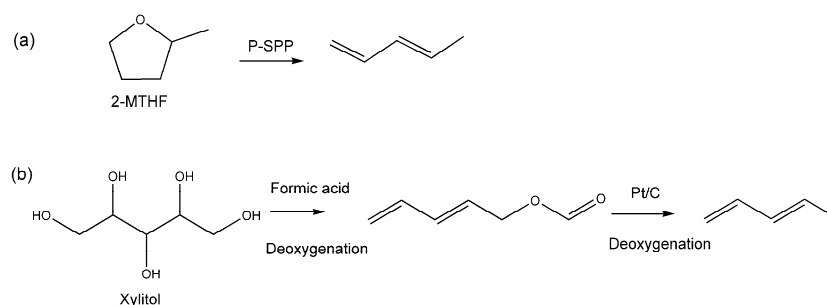


Figure 6. Synthesis of 1,3-pentadiene from 2-methyltetrahydrofuran (2-MTHF) (a) and Xylitol (b) [100,101].

4. Rigid-Group Functionalized 1,3-butadienes

4.1. Synthesis of 2-(1-adamantyl)-1,3-butadiene

Due to its highly symmetrical and rigid tricyclic structure, adamantane features chemical and thermal stability, hydrophobic character, and UV transparency. It has been introduced into polymers

to improve their thermal and mechanical properties [102–111]. Therefore, introduction of adamantyl into 1,3-dienes is explored as presented in Figure 7 [112,113].

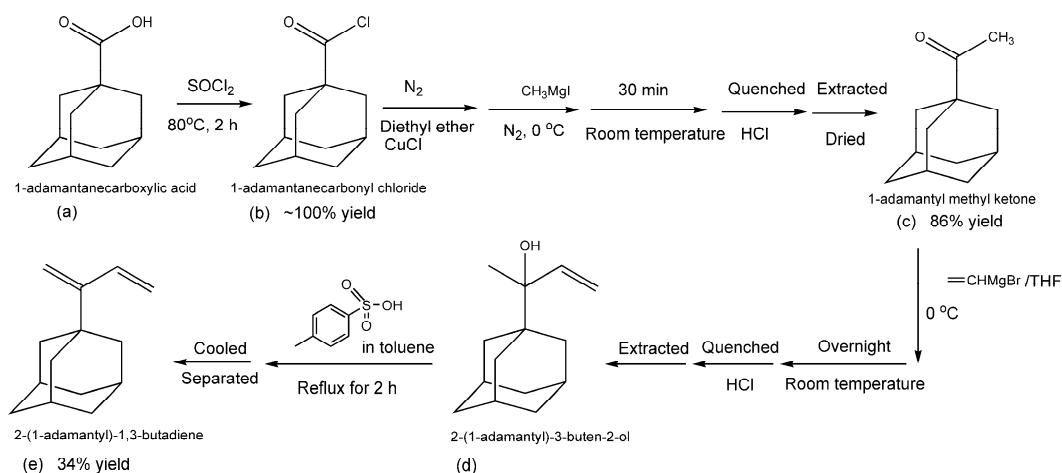


Figure 7. Synthesis of 2-adamantyl-1,3-butadiene [112,113].

Firstly, methylmagnesium iodide is prepared by adding methyl iodide and magnesium into diethyl ether. 1-Adamantanecarboxylic acid (Figure 7a) and thionyl chloride are charged into a vessel, and the mixture is heated to 80°C and then left for 2 h with stirring. After the reaction, thionyl chloride is removed to afford a white solid of 1-adamantanecarbonyl chloride (Figure 7b) under reduced pressure. Then, diethyl ether and CuCl are added to 1-adamantanecarbonyl chloride under a N_2 atmosphere, followed by the dropwise addition of methylmagnesium iodide at 0°C under a N_2 atmosphere. After stirring at room temperature for 30 min, the reaction is quenched with 2 N HCl . The mixture is extracted with diethyl ether. Then, the organic layer is dried over anhydrous MgSO_4 . After the removal of the solvent, the product (Figure 7c) is obtained. In an ice/water bath under a N_2 atmosphere, the THF solution of vinyl bromide is added dropwise to magnesium, which is activated with 1,2-dibromoethane and stirred at this temperature for another 1 h, then at room temperature for 1 h. Prior to the addition of the THF solution of the product in Figure 7c, the reaction mixture is cooled down to 0°C . Finally, stirring at room temperature overnight is maintained. The reaction is quenched with 2 N HCl , and diethyl ether is used to extract the reaction system. After the evaporation of the solution, the product (Figure 7d) is obtained. The solution of the product (Figure 7d) in benzene refluxes for 2 h in the presence of p -toluenesulfonic acid. After cooling, the organic layer is separated and dried. The solvent is removed to afford the final product (Figure 7e).

4.2. Synthesis of 2-phenyl-1,3-butadienes

2-Phenyl-1,3-butadiene (2-PB) can be regarded as either an α -vinyl-substituted styrene or 2-phenyl-substituted 1,3-butadiene. Therefore, 2-PB is a unique monomer because of the importance of styrene and 1,3-butadiene in synthetic rubbers. Moreover, with a phenyl group replacing methyl, Poly(2-PB) exhibits distinctive properties compared with polyisoprene. Moreover, Poly(2-PB) can also be used to produce high-temperature thermoplastics with a T_g as high as 325°C [114]. Since the successful synthesis of 2-PB by Marvel, [115] it received much attention [116,117].

As displayed in Figure 8, vinyl bromide and magnesium are used to prepare the THF solution of vinylmagnesium bromide, followed by the addition of acetophenone (Figure 8a). The mixture must be maintained under gentle reflux and then maintained with stirring for 1 h. A saturated aqueous solution of ammonium chloride is applied for the hydrolysis process to obtain the crude product. After the distillation and removal of the solvent, methylphenylvinylcarbinol (Figure 8b) is afforded with a yield of 75%. Methylphenylvinylcarbinol, aniline hydrobromide, and hydroquinone are charged into a round-bottomed flask equipped with a Vigreux column. The mixture is heated

at 100 °C in an oil bath, followed by gentle distillation with the temperature increasing to 150 °C. The fraction with a b.p. of 57–63 °C is collected and dried by anhydrous calcium chloride to obtain 2-PB (Figure 8c). Recently, Yao et al. [118] used acetophenone as the starting material to prepare 2-PB via elaborate manipulations, which are performed under a dried and oxygen-free atmosphere, and the solvents involved in the reaction must be purified. In the typical procedure, acetophenone is first converted into 2-phenylbut-3-en-2-ol in the presence of vinylmagnesium bromide at 0 °C, followed by a dehydration reaction to afford 2-PB in the presence of pyridinium p-toluenesulfonate at 80 °C; THF and toluene are employed as solvents, respectively. Similar to 2-PB, 1-phenyl-1,3-butadiene (1-PB) and 1-(4-methyphenyl)-1,3-butadiene (1-MPB) have also gained much attention [120–125].

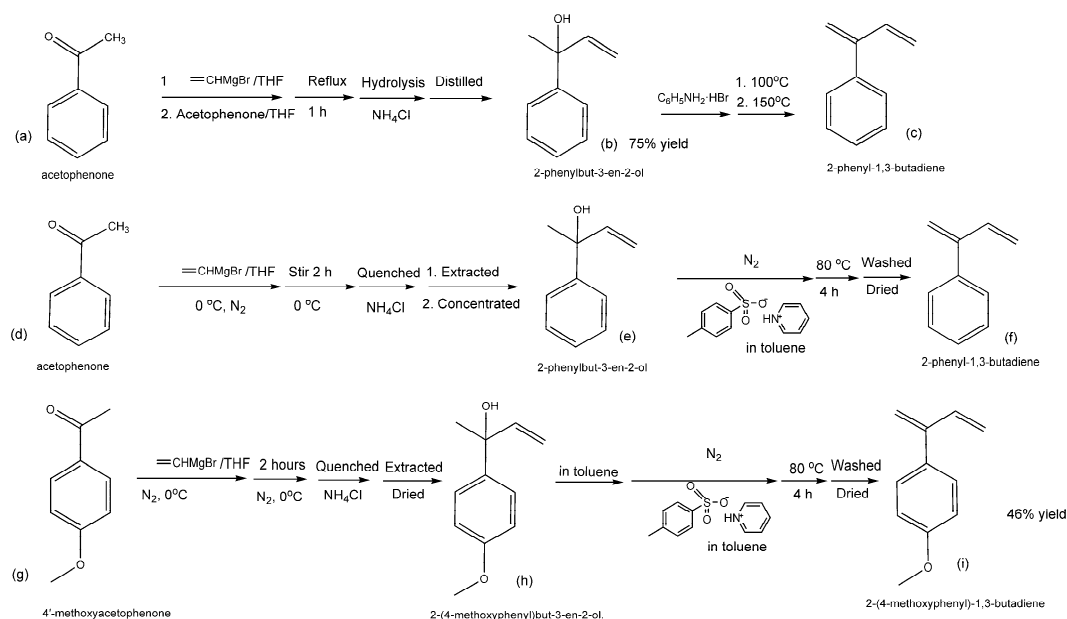


Figure 8. Synthesis of 2-phenyl-1,3-butadiene [115–119].

Moreover, Yao et al. synthesized 2-(4-methoxyphenyl)-1,3-butadiene (2-MOPB) through the dehydration of 2-(4-methoxyphenyl) but-3-en-2-ol in the presence of pyridinium p-toluenesulfonate which is used as a dehydrating agent. The manipulations were conducted under mild conditions, with a moderate yield of 46% [119]. Phenyl-1,3-butadiene derivatives provide a promising platform for the synthesis of polar-group functionalized 1,3-butadienes by introducing substituents into phenyl [126–128]. In our previous work, 4-methyl-4-phenyl-1,3-dioxane (MPD) was synthesized via Prins condensation of α -methylstyrene with formaldehyde and MPD could be easily converted into 2-PB over solid acid catalysts at above 250 °C [129]. Notably, 2-PB can hardly be modified with functional groups in the presence of a conjugated bond. However, it is possible to introduce functional groups into MPD, and then the functionalized MPD can be easily converted into functionalized 2-PB and 1-PB (Figure 9). Therefore, this is a promising candidate route for the synthesis of 2-PB with functional groups on a large scale.

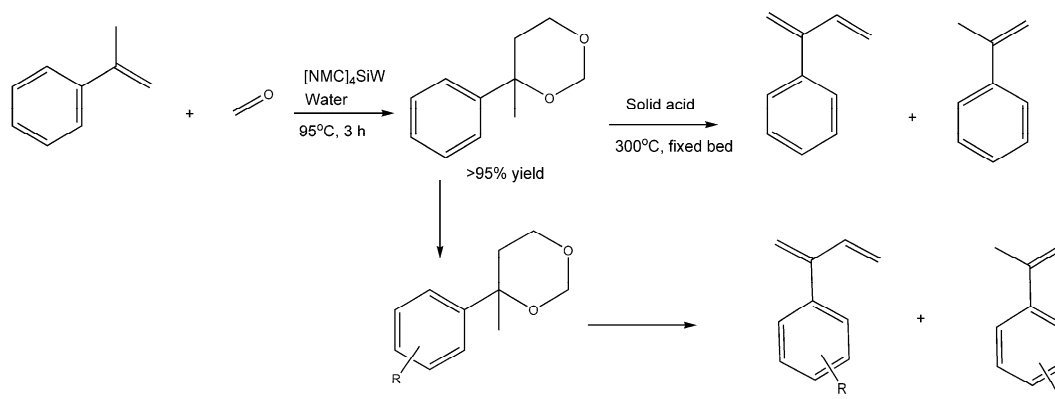


Figure 9. A straightforward way to synthesize 2-phenyl-1,3-butadiene [129].

5. Polar-Group Functionalized 1,3-butadienes

A large number of functionalized dienes with polar groups containing O, N, and Si, such as vinyloxy, ethoxymethyl, cyanomethyl, amine derivatives, alkyloxysilyl, alkylsilyl, alkyloxymethyl, N,N-dialkylamino dimethylsilyl, etc., have been reported.

2-Vinyloxy-1,3-butadiene is a potentially valuable building block and monomer, as it can be taken as either a functionalized 1,3-butadiene or vinyl ether ($\text{CH}_2=\text{CHOR}$). It has been synthesized by a hydrative trimerization reaction using acetylene and water as raw materials at 80–115 °C in the $\text{KOH}\cdot\text{H}_2\text{O}/\text{DMSO}$ system (Figure 10) [130,131]. It is suggested that one molecule of acetylene reacts with one molecule of water to form acetaldehyde (Figure 10c), which undergoes ethynylation in the presence of another molecule of acetylene to give acetylenic alcohol (Figure 10d), followed by the vinylation to afford (Figure 10e). After isomerization of acetylene-allene-diene, 2-vinyloxy-1,3-butadiene is obtained [132]. Recently, Vitkovskaya et al. studied the mechanism of this reaction by using the MP2/6-311++G**//B3LYP/6-31+G* quantum chemical framework [133,134]. They clarify that the formation of acetaldehyde and its ethynylation occur in complexes of 5DMSO·KOH, and the addition of the hydroxide ion to the acetylene molecule is the rate-determining step of this reaction.

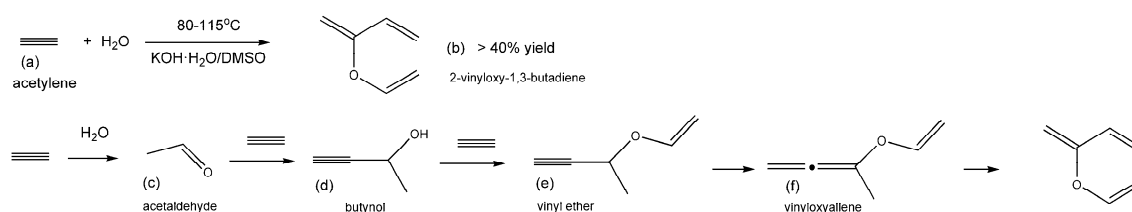


Figure 10. The pathway of synthesis of 2-vinyloxy-1,3-butadiene [130–132].

2-Ethoxymethyl-1,3-butadiene is synthesized as shown in Figure 11 [135–137]. The prepared 2-bromomethyl-1,3-butadiene (Figure 11a) is added dropwise to sodium ethoxide solution at 0 °C, followed by stirring overnight at 40 °C; 2-ethoxymethyl-1,3-butadiene (Figure 11b) is obtained after distillation under reduced pressure at a yield of 63%. Dry THF is employed as the solvent. The used 2-bromomethyl-1,3-butadiene can be synthesized as follows: firstly, bromine is added dropwise to isoprene (Figure 11h) in a dry ice/acetone bath (maintained below −20 °C) to obtain 1,4-dibromo-2-methyl-2-butene (Figure 11i) with a yield of 100%. Following the addition of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU), 1,4-dibromo-2-methyl-2-butene is converted into 2-bromomethyl-1,3-butadiene which is collected by applying a vacuum.

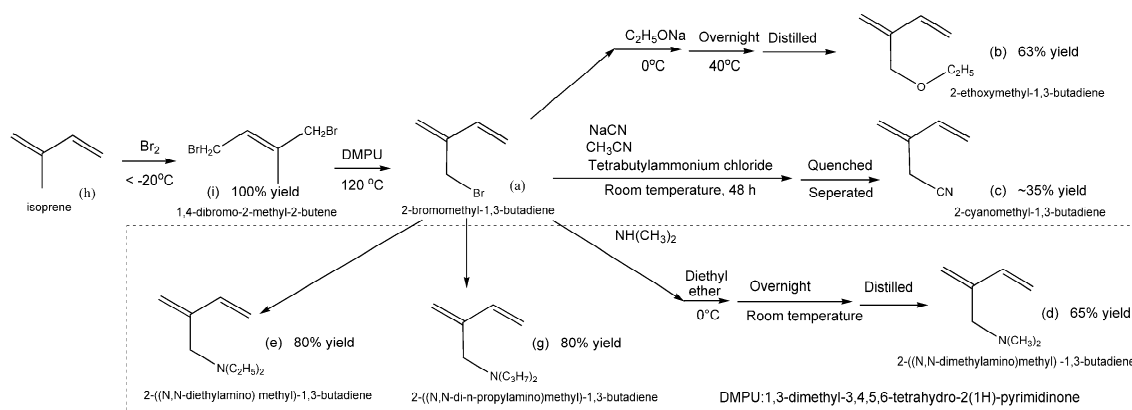


Figure 11. Synthesis of functionalized 1,3-butadiene using 2-bromomethyl-1,3-butadiene [135–144].

2-Cyanomethyl-1,3-butadiene can be used for the production of synthetic rubbers that show excellent oil and solvent resistance, as well as adhesive properties owing to the introduction of cyano into butadiene [138]. As is known, a higher acrylonitrile content in NBR can give rise to a higher resistance to hydrocarbons and impermeability to gases, but it also leads to lower resilience and temperature flexibility [145,146], which indicates that oil resistance and low-temperature flexibility are mutually incompatible. Cyano-substituted monomers could provide an ideal solution to this problem [139]. Jing et al. [138,139] synthesized 2-cyanomethyl-1,3-butadiene in three steps, with the synthesis of 2-bromomethyl-1,3-butadiene from isoprene and Br_2 via the first two steps (Figure 11). In the third step, sodium cyanide, acetonitrile, and tetrabutylammonium chloride are added into the reaction mixture. After stirring at room temperature for 48 h, the mixture is quenched, extracted, washed, and distilled to afford 2-cyanomethyl-1,3-butadiene (Figure 11c). The total yield is about 35%.

Quite different from 2-cyanomethyl-1,3-butadiene, the introduction of amine groups into dienes could remarkably change the properties of their final polymers, such as adhesion and solubility. It has been verified that the solubility of this kind of polymer in polar solvents is better than that of a polymer without polar-side chains, such as polybutadiene and polyisoprene. Moreover, the polymer containing the amine always presents chemical and structural versatility. Therefore, a lot of effort has been put into the synthesis of 1,3-butadiene containing amines (Figure 11) [140,141]. 2-((N,N-Dimethylamino)methyl)-1,3-butadiene (Figure 11d) is synthesized by adding 2-bromomethyl-1,3-butadiene dropwise into the mixture of diethyl amine and ether at 0 °C, followed by stirring overnight at room temperature. In this process, an aqueous solution of dimethyl amine (40%) is used. After distillation, a colorless liquid product is obtained with a 65% yield [142–144]. By a similar method, 2-((N,N-diethylamino) methyl)-1,3-butadiene (Figure 11e) and 2-((N,N-di-n-propylamino)methyl)-1,3-butadiene (Figure 11g) are synthesized using 2-bromomethyl-1,3-butadiene and the corresponding amines, and both of their yields can reach 80%. An alternative route is displayed in Figure 12.

The pre-prepared 2-bromomethyl-1,3-butadiene can also be synthesized as shown in Figure 13 [144]. Prior to charging condensed SO_2 as a liquid into a stainless-steel reactor, an acetone/dry ice bath is employed to maintain the mixture temperature below -10 °C. After the introduction of isoprene, methanol, and hydroquinone, the reactor is sealed and heated to 85 °C for 4 h with stirring. After cooling the mixture to room temperature, deionized water is added to allow for recrystallization of the product in Figure 13a, which is obtained with a yield of 90%. Then, the product (Figure 13a), together with N-bromosuccinimide, benzyl peroxide, and chloroform, is charged into the round-bottom flask equipped with a condenser. After refluxing for 20 h, evaporation of the solvent and recrystallization of the product are carried out to afford the product in Figure 13b with a yield of 25%. A trace amount of hydroquinone and this product (Figure 13b) are charged into a preheated flask

(170 °C) using an oil bath. After melting the solid, a vacuum is applied and the greenish-brown liquid product (Figure 13c) is gained with a yield of 80% (2-bromomethyl-1,3-butadiene).

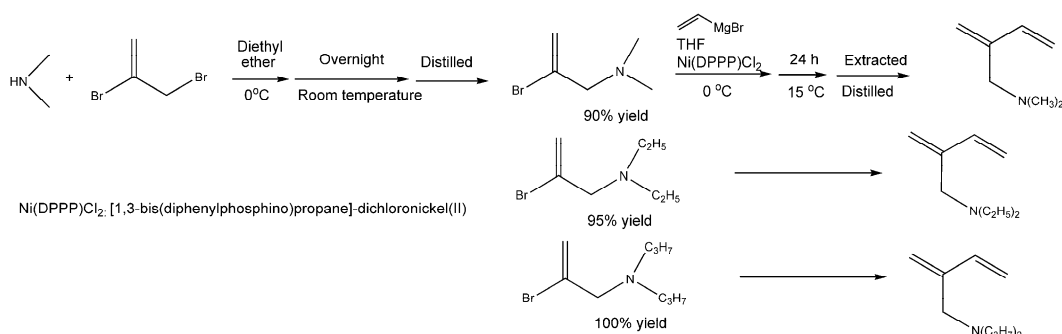


Figure 12. Alternative route for the synthesis of amine groups functionalized 1,3-butadiene [144].

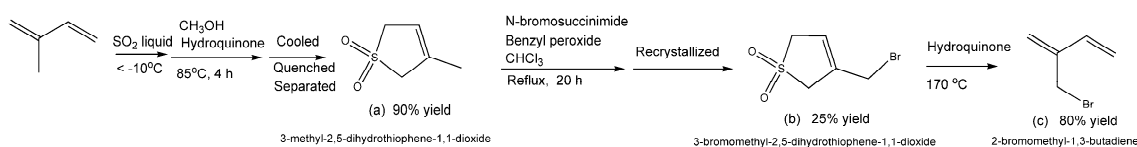


Figure 13. Synthesis of 2-bromomethyl-1,3-butadiene [144].

Sato et al. [147] reported a synthetic route of 2-(triisopropoxysilyl)-1,3-butadiene in 1984; since then, this kind of functional diene has attracted wide interest. In this route, 2-(triisopropoxysilyl)-1,3-butadiene is prepared using 1,4-dichloro-2-(trichlorosilyl)-2-butene and isopropyl alcohol as starting materials (Figure 14) [148,149]. Firstly, the solution of isopropyl alcohol in triethylamine is added dropwise to a THF solution of 1,4-dichloro-2-(trichlorosilyl)-2-butene (Figure 14a) at 0 °C. After stirring overnight at 20 °C, the mixture is heated to 60 °C and kept for several hours, followed by cooling to 0 °C. Hexane is applied to precipitate the inorganic salt, which is removed using Hyflo-Super-Cel[®] (Johns-Manville Co.). Then, 1,4-dichloro-2-(triisopropoxysilyl)-2-butene (Figure 14b) is obtained by distillation. In the second step, the THF solution of 1,4-dichloro-2-(triisopropoxysilyl)-2-butene (Figure 14b) is dropwise added to a mixture of zinc powder in THF under refluxing condition. After refluxing for 2 h, the reaction mixture is cooled down to 0 °C. In this stage, pentane is used to precipitate the inorganic salt. 2-(Triisopropoxysilyl)-1,3-butadiene (Figure 14c) is afforded with a yield of 64% after removing the salt and solvent. By a similar method, 2-triethoxysilyl-1,3-butadiene (Figure 14d) is synthesized from 1,4-dichloro-2-(trichlorosilyl)-2-butene and ethanol, and 2-(diisopropoxymethylsilyl)-1,3-butadiene (Figure 14e) and 2-(dimethylisopropoxysilyl)-1,3-butadiene (Figure 14f) are synthesized via a reaction of isopropyl alcohol with 1,4-dichloro-2-(dichloromethylsilyl)-2-butene or 1,4-dichloro-2-(dimethylchlorosilyl)-2-butene, respectively.

2-Triethoxymethyl-1,3-butadiene is synthesized by a coupling reaction of tetraethyl orthocarbonate and 2-(1,3-butadienyl) magnesium chloride (Figure 14) [150]. A THF solution of tetraethyl orthocarbonate is charged into a flask equipped with a reflux condenser. A THF solution of 2-(1,3-butadienyl) magnesium chloride is added dropwise under a N₂ atmosphere at 55–65 °C. Then the reaction mixture is stirred for 48 h. After the reaction, the mixture is concentrated and poured into a NH₄Cl solution containing ice, then extracted three times with ether. After removing the solvent, distillation is employed to attain 2-triethoxymethyl-1,3-butadiene (Figure 14j).

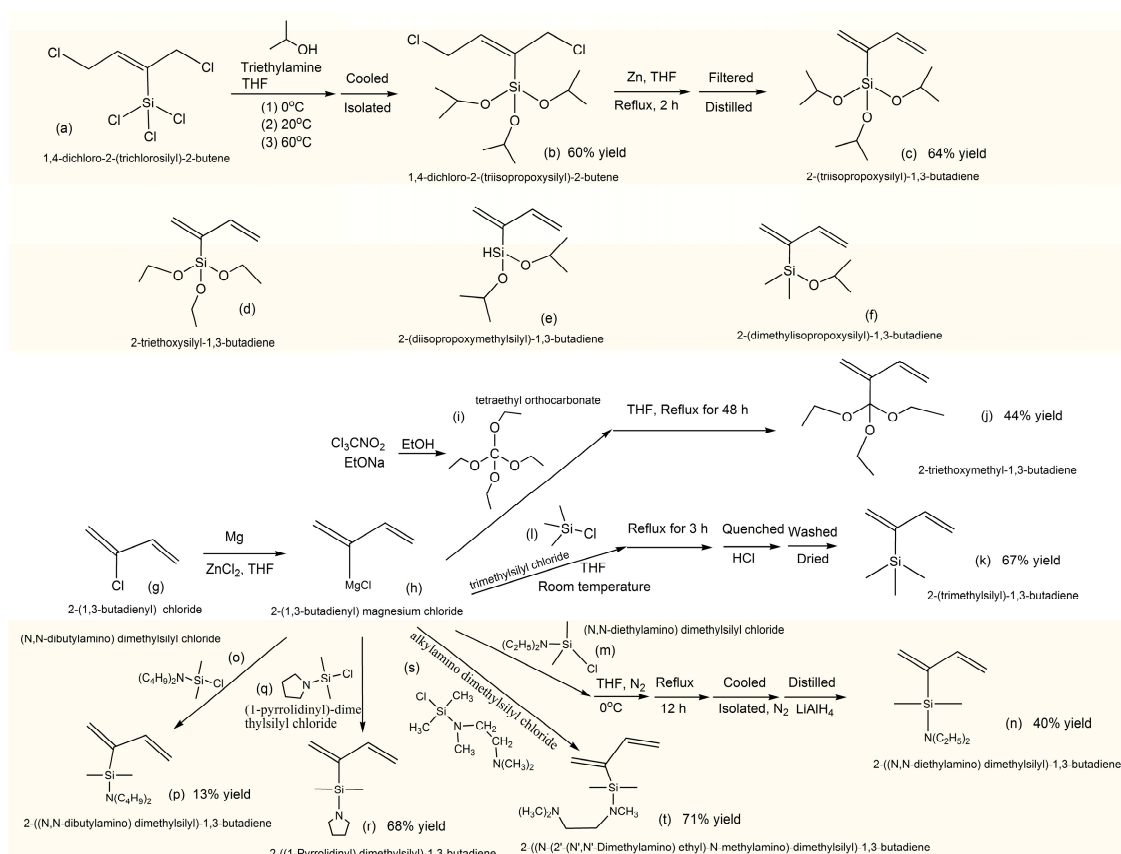


Figure 14. Synthesis of 2-substituted 1,3-butadienes [135,147–151].

2-(Trimethylsilyl)-1,3-butadiene is synthesized as given in Figure 14. Trimethylsilyl chloride is added to a solution of pre-prepared 2-(1,3-butadienyl) magnesium chloride in THF at room temperature. Then the mixture is heated and refluxed for 3 h. After the reaction, the mixture is poured into 2 N HCl and extracted with pentane. After removing the solvent, 2-(trimethylsilyl)-1,3-butadiene is obtained (Figure 14k). The synthesis of pre-prepared 2-(1,3-butadienyl) magnesium chloride has been described elsewhere [151].

2-(N,N-Dialkylamino)dimethylsilyl-1,3-butadienes are synthesized by the reactions of 1,3-butadien-2-ylmagnesium chloride with the corresponding (N,N-dialkylamino)dimethylsilyl chloride (Figure 14) [135]. In typical procedures, 2-((N,N-diethylamino) dimethylsilyl)-1,3-butadiene (Figure 14n) is synthesized by dropwise adding a solution of (N,N-diethylamino) dimethylsilyl chloride (Figure 14m) to 1,3-butadien-2-ylmagnesium chloride (Figure 14h) under an atmosphere of nitrogen at 0 °C. THF is used as the solvent. Followed by refluxing for 12 h, the mixture is cooled, filtered, and washed with a solution of dry pentane/THF under a nitrogen atmosphere. After evaporation and distillation over LiAlH₄, 2-((N,N-diethylamino) dimethylsilyl)-1,3-butadiene is afforded as a colorless liquid with a yield of 40%. According to similar procedures, (N,N-dibutylamino) dimethylsilyl chloride (Figure 14o), (1-pyrrolidinyl)-dimethylsilyl chloride (Figure 14q), and (N-(2'-(N',N'-dimethylamino) ethyl)-N-methylamino)dimethylsilyl chloride (Figure 14s) are used to synthesize 2-((N,N-dibutylamino) dimethylsilyl)-1,3-butadiene (Figure 14p) at a 13% yield, 2-((1-Pyrrolidinyl) dimethylsilyl)-1,3-butadiene (Figure 14r) at a 68% yield, and 2-((N-(2'-(N',N'-Dimethylamino) ethyl)-N-methylamino)-dimethylsilyl)-1,3-butadiene (Figure 14t) at a 71% yield. Moreover, 1,3-butadienes with abundant functional groups at the 2-position have been reported (Figure 15) [152,153].

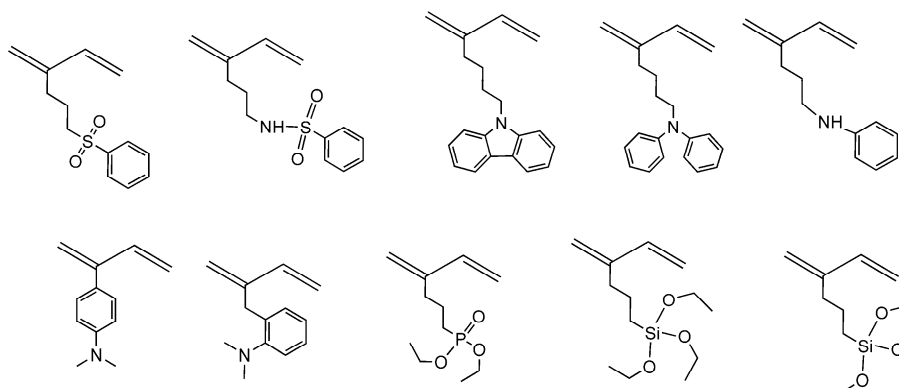


Figure 15. Reported 2-substituted 1,3-butadienes [152,153].

6. Conclusions and Outlook

1,3-Butadienes (especially IB and IP) are the basic building blocks for the synthetic rubbers used in the tire fabrication industry, and it is needless to mention that their production still depends on petrochemicals in industry. Taking into consideration the depletion of oil reserves, the volatile price of petrochemicals, and the issues related to the environment, it is urgent to explore renewable resources for the sustainable production of 1,3-butadienes, especially for those in large demand in the industry [88,154,155]. The production of 1,3-butadienes from biomass-derived feedstocks is a prospective route, which is increasingly competitive in polymer production [156]. With regards to sustainability, great achievements have been obtained in the production of IB from ethanol in both academia and the industry. Unfortunately, it is still a great challenge to improve the BD yield and to develop robust catalysts because the aldol coupling and the dehydrogenation steps involved in this technology cannot be efficiently performed on simple metal oxide catalysts [157].

Bio-derived C4 alcohols and especially unsaturated C4 alcohols have been declared promising feedstocks for the production of BD via the dehydration process; even the two-step synthesis of BD from C4 alcohols via UOLs displays a total BD yield of 96.6% over Yb_2O_3 at 360 °C. A great deal of work still needs to be done, especially for the improving catalyst life for industry usage. For the sustainable production of IP, a lot of efforts must be made. Although some biomass-derived chemicals, such as itaconic acid, have been explored in the last 2 years, it is still difficult to meet the requirements for industrial-scale production. Extensive research studies on IP synthesis are urgently required, and the exploration of novel platform chemicals faces challenges but will be highly rewarding. Fortunately, the US Department of Energy (DOE) “Top 10” report (the DOE outlined research needs for bio-based products in 2004) and its revision provide guidance to choose potential candidate chemicals for IP synthesis, as well as BD [158–160].

In contrast, functionalized 1,3-butadienes, without any research on their synthesis from biomass-derived chemicals, are always synthesized at the lab scale by complicated operations under rigorous conditions, e.g., without water or oxygen, such as the synthesis of these monomers with phenyl, silicon, cyano, and amino groups. However, they play an essential role in enhancing the existing properties of synthetic rubber, particularly for certain special applications. Therefore, exploration of a simple catalytic route to synthesize functionalized-1,3-butadienes at a large scale is still needed. In China, research work is ongoing in this direction at the Key Laboratory of High-Performance Synthetic Rubber and its Composite Materials, Changchun Institute of Applied Chemistry, CAS and is expected to continue in the next few years.

Author Contributions: Y.Q. performed the literature search and drafted the manuscript; Z.L. and C.B. made great efforts to revise the manuscript; S.L., L.C., Q.D., J.H., and W.D. participated in the checking of this work.

Funding: This work was supported by the National Natural Science Foundation of China (No. 51873203); National Natural Science Foundation of China (No. 51473156); Key Projects of Jilin Province Science and Technology

Development Plan (No. 20160204028GX); and Key Projects of Jilin Province Science and Technology Development Plan (No. 20180201087GX).

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

1,3-BDO	1,3-Butanediol
1,4-BDO	1,4-Butanediol
1-MPB	1-(4-Methypenyl)-1,3-butadiene
1-PB	1-Phenyl-1,3-butadiene
2,3-BDO	2,3-Butanediol
2B1OL	2-Buten-1-ol
2-MOPB	2-(4-Methoxyphenyl)-1,3-butadiene
2-MTHF	2-Methyltetrahydrofuran
2-PB	2-Phenyl-1,3-butadiene
3B1OL	3-Buten-1-ol
3B2OL	3-Buten-2-ol
3-MTHF	3-Methyltetrahydrofuran
BD	1,3-Butadiene
BDOs	Butanediols
BR	Butadiene rubber
CR	Chloroprene rubber
DMD	4,4-Dimethyldioxane-1,3
IP	Isoprene
IR	Isoprene rubber
MPD	4-Methyl-4-phenyl-1,3-dioxane
MTBE	Methyl tertiarybutyl ether
MVK	Methyl ethyl ketone
NBR	Nitrile butadiene rubber
NB	Natural rubber
SBR	Styrene butadiene rubber
Tg	Glass transition temperature
THF	Tetrahydrofuran
UOLs	Unsaturated C4 alcohols

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