



Review

Industrial applications of olefin metathesis

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Abstract

Olefin metathesis opens up new industrial routes to important petrochemicals, oleochemicals, polymers and specialty chemicals. The most important applications of olefin metathesis in the field of petrochemicals are the olefins conversion technology (OCT) process (originally the Phillips triolefin process) and the Shell higher olefins process (SHOP).

In particular, naphtha steam crackers with an integrated metathesis unit are an interesting alternative for producing propene via the OCT process, as a high global demand for propene outpaces supply from conventional sources. In the polymer field, ring-opening metathesis polymerisation (ROMP) of cycloalkenes is an attractive process for making polymers possessing special properties. Several industrial processes involving ROMP have been developed and brought into practice, such as the ROMP of cyclooctene, norbornene and dicyclopentadiene, leading to useful polymers. Metathesis of natural fats and oils and their derivatives offers possibilities for future developments in the oleochemical industry, providing a contribution to a sustainable chemical industry. Moreover, in the light of the new metal–carbene metathesis catalysts, in particular the functional-group-tolerant well-defined ruthenium-based catalysts, it is to be expected that in the fine chemistry the metathesis reaction will soon find its way as a tool for the synthesis of agrochemicals, insect pheromones, fragrances, pharmaceutical intermediates, etc. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

Olefin metathesis is one of the very few fundamentally novel organic reactions discovered in the last 40 years. Among others, it opens up new industrial routes to important petrochemicals, polymers, oleochemicals and specialty chemicals.

At Phillips Petroleum Co. this reaction was discovered serendipitously by Banks and Bailey 40 years ago, when they were seeking an effective heterogeneous catalyst to replace the HF acid catalyst for converting olefins into high-octane gasoline via olefin–isoparaffin alkylation [1]. When using a supported molybdenum catalyst, they found that, e.g. instead of alkylating the paraffin, the olefin molecules were split, and discovered that propene can be catalytically converted into ethene and butene.

Since then, industrial applications of the olefin metathesis reaction, including ring-opening metathesis polymerization, enjoyed increasing interest, in particular in recent years. Here I will present an overview of the present situation. Pro-

cesses known until 1997 have also been described elsewhere, including processes that are no longer commercial [2].

2. Industrial processes for the production of normal olefins*2.1. Production of propene*

Propene is obtained mainly from naphtha steam crackers (globally about 65%) as a co-product with ethene, and as a co-product from gasoline-making from fluid catalytic cracking (FCC) units at refineries. Relatively small amounts are produced by propane dehydrogenation and by coal gasification via Fischer–Tropsch chemistry. Strong global demand for propene, however, presently outpaces supply from these conventional sources. Propene is used for about 60% for making polypropene, and further for producing acrylonitrile, oxo alcohol, acrylic acid, etc.

2.1.1. The Phillips triolefin process

An alternative route to propene is by applying the metathesis reaction for the conversion of a mixture of ethene and

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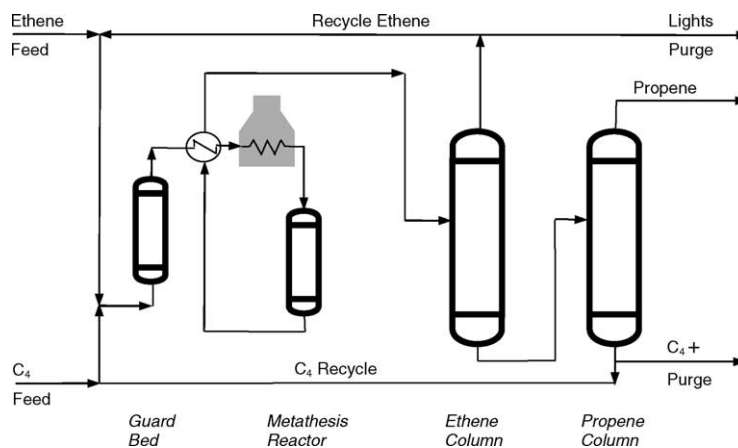


Fig. 1. The OCT process (reversed Phillips triolefin process) [3].

2-butene into propene. This process, called the Phillips triolefin process, which utilizes a heterogeneous catalyst system, was originally developed by Phillips Petroleum Co., USA, and operated from 1966 to 1972 for the conversion of propene into ethene and butene, due to less propene demand at that time. The Phillips process in the reverse direction, Eq. (1), is now offered by ABB Lummus Global, Houston (USA), for license as olefins conversion technology (OCT) for the production of propene.



Fig. 1 shows a simple process flow diagram of the OCT process. Fresh C_4 's plus C_4 recycle are mixed with ethene feed plus recycle ethene and sent through a guard bed to remove trace impurities from the mixed feed. The feed is heated before entering the metathesis reactor. The reaction takes place in a fixed-bed reactor over a mixture of WO_3/SiO_2 (the metathesis catalyst) and MgO (an isomerization catalyst) at $>260^\circ\text{C}$ and 30–35 bar [3]. 1-Butene in the feedstock is isomerized to 2-butene as the original 2-butene is consumed in the metathesis reaction.

The conversion of butene is above 60% per pass and the selectivity for propene is $>90\%$. The reactor is regenerated on a regular basis [4].

In 1985, the Lyondell Petrochemical Co. started to operate a plant in Channelview, Texas (USA) for the production of 136,000 t per year of propene. In their process, part of the ethene from ethane-cracking units is dimerized to 2-butene, using a homogeneous nickel catalyst developed by Phillips, which reacts with the rest of the ethene to produce propene [5]. The process has been retrofitted to the company's steam cracker in Channelview [6].

In particular, naphtha steam crackers with an integrated metathesis unit are an interesting alternative for producing more propene. In December 2001, BASF FINA Petrochemicals (a 60–40 joint venture between BASF and Atofina) brought on stream a world-scale steam cracker plant in Port Arthur, Texas (USA), which will integrate the OCT process to enhance the production of propene in relation to

ethene. This plant produces 920,000 t per year of ethene and 550,000 t per year of propene, but when the metathesis unit is added (early 2004), it will adjust the output to 830,000 t per year of ethene and 860,000 t per year of propene [7]. Raw C_2 and C_4 feedstocks are supplied directly by the steam cracker, but additional C_4 's will be taken from the Sabina Chemicals' C_4 splitter being planned by a joint venture of Shell Chemicals, BASF and Atofina; by-products are recycled to the cracker.

Mitsui Chemicals will install the OCT technology to meet increasing propene demand in Asia. The propene capacity of its olefins plant at its Osaka Works in Japan will be increased by 140,000 t per year from 280,000 to 420,000 t per year. Completion of the project is expected in August 2004. The new unit will be the first plant installation in Japan to produce propene using the OCT technology [8]. By this revamp, the propene to ethene production ratio can be raised from 0.6 to >1.0 .

The OCT process will also be used at Shanghai Secco Petrochemical, a joint venture of BP Chemical, Sinopec and Shanghai Petrochemical Corporation, which is building a 900,000 t per year naphtha cracker integrated with an OCT unit to produce a total of 590,000 t per year of propene at Caojing, China. The complex is scheduled for start-up in the first half of 2005 [9].

PCS (Petrochemical Corp., Singapore), a joint venture between Shell Chemicals and Sumitomo Chemical, will use OCT metathesis technology to increase the propene output at its olefin units by 200,000–300,000 t per year [10,11].

Nippon Petrochemicals plans to increase the propene capacity at its cracker with 100,000 t per year, most likely using metathesis technology [11].

2.1.2. The Meta-4 process

The Institut Français du Pétrole (IFP) and the Chinese Petroleum Corporation (Kaoshiang, Taiwan) have jointly developed a process for the production of propene, called Meta-4. In their process, ethene and 2-butene react with each other in the liquid phase in the presence of a $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$

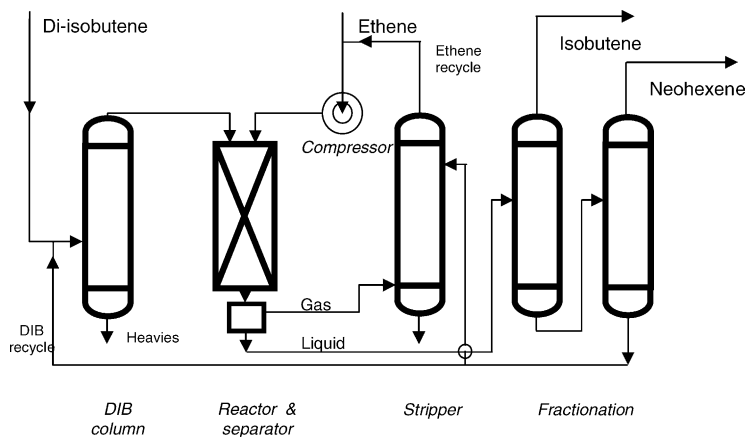


Fig. 2. The neohexene process; DIB: di-isobutene [15].

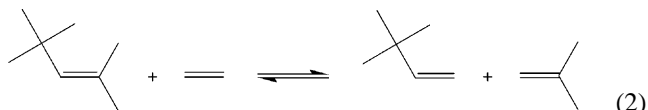
catalyst at 35 °C and 60 bar. The (equilibrium) conversion is 63% per pass [12,13]. The process is not yet commercialized, mainly because of the cost of the catalyst and the requirement of a high purity of the feed stream. This metathesis technology is presently offered by France's Axen, a subsidiary of IFP, formed in 2001 through the merger of IFP's licensing division with Procatalyse Catalysis & Adsorbents.

2.2. Production of 1-hexene

A semi-works unit using the OCT process for the metathesis of butene to produce 3-hexene, which is then isomerized into 1-hexene (a high-value comonomer used in the production of polyethylene), together with ethene and propene, is under construction at Sinopec's olefin plant in Tianjin (China), and will be started up in 2003 [14].

2.3. Production of neohexene

Neohexene (3,3-dimethyl-1-butene) is an important intermediate in the synthesis of Tonalide[®], a synthetic musk perfume. It is also used to make Terbinafine[®], an anti-fungal agent. A neohexene unit located within Chevron Phillips Chemical Company LP's Houston Chemical Complex was built in 1980 with a capacity of 1400 t per year [15]. The process is based on the dimer of isobutene, which consists of a mixture of 2,4,4-trimethyl-2-pentene and 2,4,4-trimethyl-1-pentene. Cross-metathesis of the former with ethene yields the desired product (Eq. (2)). The latter is not wasted since a dual catalyst can be used to ensure that it is isomerized to 2,4,4-trimethyl-2-pentene as this gets used up by metathesis.



With a 1:3 catalyst mixture of WO₃/SiO₂ and MgO an average conversion of the di-isobutene of 65–70% and a

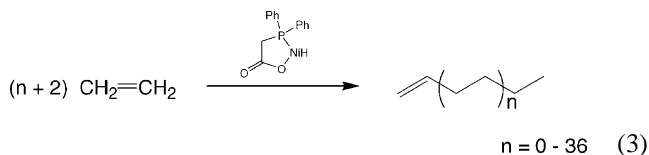
selectivity to neohexene of ~85% is achieved at 370 °C and 30 bar (molar ratio ethene/di-isobutene = 2). The co-product isobutene is recycled to an isobutene dimerization reactor.

Fig. 2 shows the process scheme of the neohexene process. Commercial di-isobutene is first fractionated to remove an oxidation inhibitor, which would otherwise poison the dual catalyst system. The fractionated di-isobutene along with the ethene stream enters the top of the reactor containing the catalysts. The ethene, consisting of make-up and recycled ethene, is compressed to the required pressure before it enters the reactor. The separation of reactants and products is achieved by stripping and fractionation. The catalyst is reactivated from time to time, using a mixture of air and inert gas to control the temperature of the coke burn-off.

2.4. The Shell higher olefins process (SHOP)

A large-scale industrial process incorporating olefin metathesis is the Shell higher olefins process (SHOP) for producing linear higher olefins from ethene. The process takes place in three stages.

In the first step, ethene is oligomerized in the presence of a homogeneous nickel–phosphine catalyst (at 90–100 °C and 100–110 bar) in a polar solvent (1,4-butanediol) to give a mixture of linear even-numbered α -olefins ranging from C₄ to C₄₀ with a Schulz–Flory type of distribution; Eq. (3). The catalyst is prepared in situ from a nickel salt, e.g. nickel chloride, and a chelating phosphorous–oxygen ligand by reduction with sodium boron hydride.

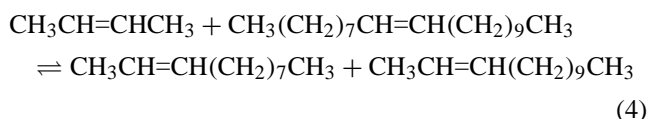


The olefins formed are immiscible with the solvent; product and catalyst phases are thereby readily separated so that the Ni catalyst can be recycled repeatedly. The C₆–C₁₈

1-alkenes are separated from the product mixture by distillation. This fraction can be further fractionated into individual compounds, which can be used as comonomer in polyethylene production or converted into products such as synthetic lubricants, plasticizer alcohols, detergent alcohols, synthetic fatty acids, etc. The remaining lighter (<C₆) and heavier (>C₁₈) alkenes go to purification beds, which remove catalyst and solvent residues that would otherwise deactivate the isomerization catalyst.

In the second step, these lighter and heavier alkenes undergo double-bond isomerization over a solid potassium metal catalyst to give an equilibrium mixture of internal alkenes.

In the third step, this mixture is passed over an alumina-supported molybdate metathesis catalyst, resulting in a statistical distribution of linear internal alkenes with both odd and even numbers of carbon atoms via cross-metathesis reactions such as reaction (4). This yields about 10–15 wt.% of the desired C₁₁–C₁₄ linear internal alkenes per pass, which are subsequently separated by normal distillation.



The isomerization and metathesis catalysts operate at 100–125 °C and 10 bar. The remaining lower (<C₁₁) and higher (>C₁₄) alkenes are recycled. The product consists of >96% of linear internal C₁₁–C₁₄ alkenes. These can then be converted into detergent alcohols, via a hydroformylation process, or into detergent alkylates [16,17].

Shell Chemicals operates a SHOP unit at Stanlow (UK) with a capacity of 270,000 t per year and three large-scale SHOP units at Geismar, Louisiana (USA) with a total capacity of 920,000 t per year of higher olefins. The third SHOP unit at their Geismar location was brought on stream in 2002 for the production of 320,000 t per year of higher olefins. This expansion brought Shell Chemicals' total worldwide production capacity to 1,190,000 t of linear alpha and internal olefins per year; these are sold under the trade name Neodene[®] [18].

2.5. Production of α -olefins

In South Africa, Sasol Ltd. is using the Fisher–Tropsch process for making olefins from synthesis gas, which can come from coal or natural gas. One of the characteristics of Fischer–Tropsch synthesis is insufficient selectivity. Efforts have to be made to bring the products obtained in line with the market requirements. Based on existing and suggested process technologies, applications of the olefin metathesis reaction to convert less desirable olefins to more useful ones are under consideration. An example of the conversion of low value olefins to high value olefins that can be employed in further downstream processes, is the conversion of low value C₇ α -olefins to internal C₁₂ olefins, which can

be used as detergent alcohol feedstock. Besides the normal heterogeneous (tungsten) catalysts for the metathesis of such α -olefins, the highly active ruthenium complexes are very attractive, due to their robustness to air, water and oxygenates, high reaction rates and selectivities. An extremely active ruthenium-based catalyst is the second-generation Grubbs-type catalyst [RuCl₂(=CHPh)(H₂IPr)(PCy₃)] with a turnover number (TON) of >640,000 at ambient temperature for the metathesis of 1-octene, and an initial turnover frequency (TOF) exceeding 3,800 s⁻¹ at 60 °C [19]. This high activity is because of the steric bulk of the ligand and superior electron-donating properties. Therefore, non-productive metathesis of the internal olefin formed during the reaction is less possible due to this increased steric bulk, which also might slow down decomposition pathways.

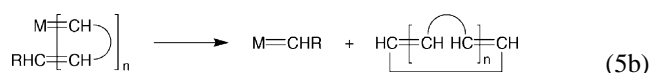
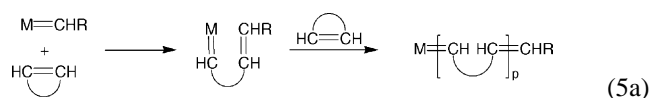
A point of high interest is that degradation products of these ruthenium catalysts can be highly active and selective double-bond isomerization and hydrogenation catalysts. In this way via, e.g. first isomerization and then metathesis, interesting conversions of low-value olefins to high-value olefins can be accomplished [20,21].

3. Industrial processes for the production of polymers

In the polymer field ring-opening metathesis polymerization (ROMP) of cycloalkenes is an attractive process for making linear polymers when based on cheap monomers or possessing special properties compensating for a high price. Several industrial processes involving homogeneously catalyzed ROMP have been developed and brought into practice. See also the book of Dragutan and Streck [22].

3.1. Polyoctenamer

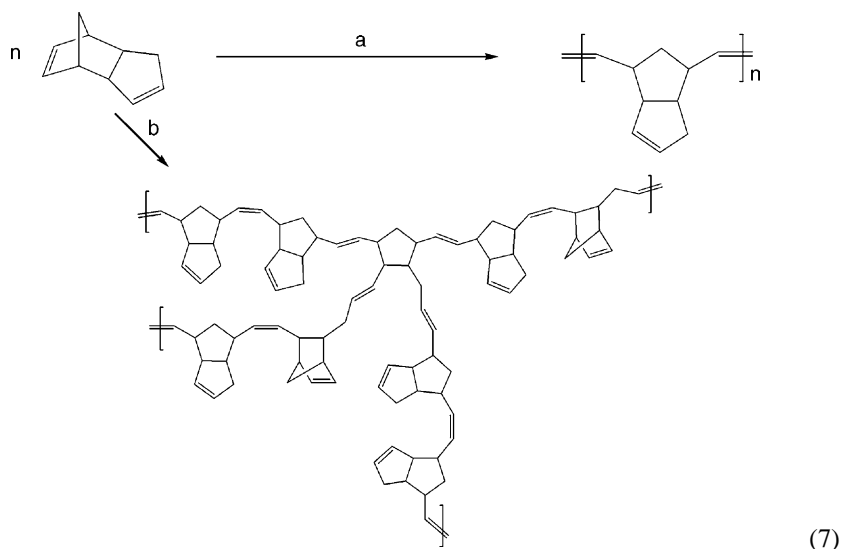
Since 1980, Degussa-Hüls AG has been producing Vestenamer[®] 8012, the metathetical polymer of cyclooctene. This polymer also goes under the name TOR (*trans*-polyoctenamer). The polymerization is performed in hexane as a solvent in the presence of a WCl₆-based catalyst, giving almost 100% yield. The polymer consists of two distinct parts: a high-molecular weight fraction (molecular weight > 10⁵) and a low-molecular weight fraction (25 wt.%) consisting of a series of cyclic oligomers. This is readily explained in terms of a competition between a propagation reaction (5a) and an intramolecular backbiting metathesis reaction (5b).



The product has a purity of 99.5%. The *cis* to *trans* ratio, which determines the degree of crystallinity, is con-

trolled by the polymerization conditions. The *trans* double bond content of Vestenamer[®] 8012 is 80%, the crystallinity 30%, and the molecular weight 75,000. Used as a blending material, it offers possibilities for the improvement of

ring opened, a linear polymer should be formed; Eq. (7a). However, under certain conditions the double bond in the disubstituted cyclopentene ring may also undergo metathesis, thereby giving rise to cross-linking; Eq. (7b).

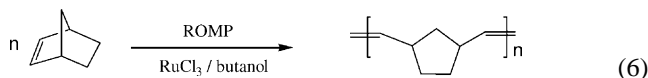


properties of rubber compounds and for use in rubberized asphalt. An additional type, Vestenamer[®] 6213, with a lower *trans* content (60%) and, therefore, lower crystallinity (10%), has been developed to provide for low-temperature applications where the admixture of the standard type would lead to excessive stiffening [23,24].

3.2. Polynorbornene

The first commercial metathesis polymer was polynorbornene, which was put on the market in 1976 by CdF-Chimie in France, and in 1978 in the USA and Japan, under the trade name Norsorex[®] [25].

The polymer is obtained by ROMP of 2-norbornene (bicyclo[2.2.1]-2-heptene), the Diels–Alder product of dicyclopentadiene and ethene, and gives a 90% *trans* polymer with a very high molecular weight ($> 3 \times 10^6$ g/mol) and a glass transition temperature (T_g) of 37 °C (Eq. (6)). The process uses a RuCl_3/HCl catalyst in butanol, operates in air, and produces a useful elastomer, to be used for oil spill recovery, as a sound barrier, or for damping.



Norsorex[®] is presently produced in Carling (France) by Atofina, and developed worldwide by the Japanese company Nippon Zeon.

3.3. Polydicyclopentadiene

Much interest has been shown in the ROMP of *endo*-dicyclopentadiene (DCPD), obtained as a by-product from naphtha crackers. If only the highly strained norbornene

The product is a tough, rigid, thermoset polymer of excellent impact strength. Quite large objects can be produced via a reaction injection molding (RIM) process. The commercial production of molded objects from DCPD-based feed using RIM technology has been developed mainly by the BFGoodrich Co., under the trade name Telene[®], and by Hercules Inc. under the trade name Metton[®]. The latter is now produced by Metton America, Inc. at La Porte (USA) and Teijin-Metton Co. in Japan.

In the RIM technique, two monomer streams are used. In the Metton[®] liquid molding resin (LMR) system developed by Hercules, one stream contains DCPD monomer, catalyst ($\text{WCl}_6 + \text{WCl}_4$), nonylphenol (to solubilize the tungsten compounds in the monomer), additives (such as antioxidants), and fillers. The other stream contains DCPD monomer, cocatalyst (EtAlCl_2), retarder, additives and fillers. The two streams pass first into a mixing chamber and then into the mold, where an exothermic polymerization takes place at a high rate after a short induction period. The solutions of the individual catalyst components in the monomer are stable, and the length of the induction period can be controlled [26].

In the Telene[®] process the procatalyst is a tetrakis(tridodecylammonium)octa-molybdate, activated with a mixture of Et_2AlCl , propanol and SiCl_4 . Up to 10% trimer of cyclopentadiene is added to the monomer to increase cross-linking in the polymer, while the trimer also lowers the melting point of DCPD. The T_g of the product is typically 150 °C. BFGoodrich Co. have licensed their process to Cymetech (USA) and to Nippon Zeon, which produces it under the trade name Pentam[®].

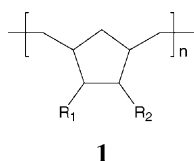
Poly-DCPD has won several marine, recreational vehicle and heavy-vehicle applications around the world, such as

heavy-truck hoods, tonneau covers for pick-up trucks, snowmobile hoods, tractor fenders, auto bumpers, etc. [27].

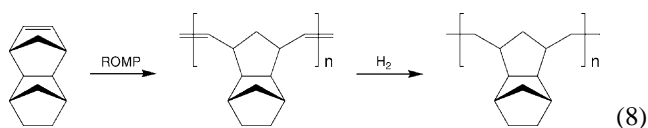
The technology using the well-defined Grubbs ruthenium catalyst is made available for poly-DCPD production by Materia (Pasadena, CA, USA) [28]. Ruthenium-based RIM poly-DCPD does not have odor problems due to residual DCPD monomer in molded parts, and the catalyst is less sensitive to air and moisture. Materia produces plastics used in sporting goods, but has licensed some of the sporting goods area to Easton Sports. Cymetech also uses the technology of DCPD polymerization based on ruthenium catalysis to produce polymers under the trade name Prometa[®]. In Japan, Hitachi Chemical Co. is marketing the polymer produced by the ruthenium catalyst technology of Cymetech under the trade name Metathene[®].

3.4. Hydrogenated polymers

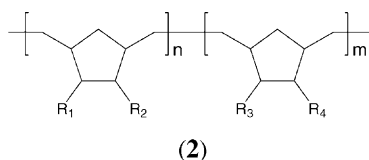
Since 1991, Nippon Zeon has been producing the polymer Zeonex[®], of the general type 1, obtained by ROMP of norbornene and related (multi-ring) monomers, followed by partial or total hydrogenation.



Eq. (8) gives an example starting with tetracyclodecene (TCD). Zeonex[®] is an amorphous, colorless and transparent polymer with a high T_g (140 °C) and low moisture absorption. These properties make it very suitable for optical applications (disks, lenses and camera prisms).



Zeonor[®] (2) is an amorphous hydrogenated co-polymer and has been commercialized since 1998. It has been accepted for use in optical, electronics and automobile applications.



4. Other commercial applications

Symrise (Germany) is making cyclohexadecadiene by metathesis of cyclooctene in the presence of a heterogeneous rhenium oxide catalyst. The cyclohexadecadiene is

then converted to the fragrance Globanone[®] (cyclohexadecene).

Materia Inc. (CA, USA) is using ruthenium-catalyst technology for the manufacture of fine chemicals. Examples are the insect pheromones of the peach twig borer (PTB, starting materials 1-hexene and 5-hexenyl acetate), and the omnivorous leafroller (OLR, key starting materials 3-hexene and 11-eicosenyl acetate, derived from jojoba oil) [29]. And also the mosquito oviposition pheromone (MOP, key starting materials 11-docosene and methyl 5-eicosenoate, derived from meadowfoam oil) [30]. Pheromones are important bio-rational alternatives to chemical pesticides.

5. Applications in the oleochemical industry

Not only in the petrochemical industry, but also in the oleochemical industry there are many interesting possibilities for olefin metathesis. The metathesis of unsaturated natural fats and oils and their derivatives offers new synthesis routes from cheap feedstocks to valuable new or existing chemical products from renewable resources with high chemo-selectivity [31,32]. Efficient homogeneous and heterogeneous catalysts have been developed and it is to be expected that their use will lead to commercial applications for the production of polymers, agrochemicals, pheromones, fragrances, pharmaceutical intermediates, etc.

6. Conclusions

In the chemical process industry, olefin metathesis has now become a process with large-scale applications using heterogeneous as well as homogeneous catalysts systems. More commercial applications are to be expected, in particular considering the recent development of highly active ruthenium metathesis catalysts that are more tolerant to functional groups and resistant towards moisture and oxygen. In the area of fine chemicals, through major advances in catalyst design in recent years, valuable products will be commercially synthesized in the (near) future via metathesis reactions, such as biologically active compounds (e.g. pharmaceuticals, insect pheromones, prostaglandins, etc.) and advanced polymeric materials via ROMP. Moreover, the metathesis reaction has also favorable perspectives for application in the oleochemical industry, and in this respect has good prospects as a contribution to a sustainable chemical industry.

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