Chapter 8
Continuously Operated Telomerisations with Renewables in Miniplants

Arno Behr and Andreas J. Vorholt

Process development of new chemicals always starts in the laboratory in discontinuous, i.e. batch experiments. When all important reaction conditions are checked and sufficient results concerning yield, selectivity, and catalyst activity are obtained, a first economic feasibility study is carried out to clarify whether the new product should be produced commercially. If this study is positive, the scale-up of the product begins. This scale-up can be done in different ways:

Originally, an "**integrated pilot plant**" was constructed with a scale-up factor of about 10^3. When the product is synthesised in the laboratory in amounts of 10–100 g, the continuously operated pilot plant is designed for the production of 10–100 kg/h. Therefore, this plant has to be built with relatively big machines and devices, which must be constructed individually by special equipment manufacturers. This makes the pilots plants relatively expansive, and the construction of the facilities takes a long time—possibly several months or even a year. When the pilot plant is ready, the following operation time is relatively long since big amounts of chemicals must be handled.

The second, more modern possibility in scale-up is the use of "**miniplants**" [1, 2]. In this case, the increase in apparatus size is only low, but again the plant works in a continuous way. The production of the new chemical is done in a scale of 10 g/h to at most 1 kg/h. Using this technique, the miniplant can be constructed with common, purchasable laboratory equipment like steel or glass reactors of dimensions of 0.5–2 L. In addition, pumps, thermostats, cryostats, controllers, valves, or pipes can be easily purchased without a special construction of expensive purpose-built items. The construction time of a miniplant often lasts only 3–4 months. The operation of the miniplant and possible reconstructions can be carried out, easily. Thus, the use of the miniplant technique is relatively cheap and provides quick but accurate results.

In homogeneous catalysis, the great advantage of miniplants is the easy check of the catalyst lifetime in a small scale. Different catalysts can be investigated successively, and the costs of operation are low. In a miniplant, all recycling streams can be closed, and the influence of accumulations on the catalyst can be

A. Behr and A.J. Vorholt, *Homogeneous Catalysis with Renewables*,
Catalysis by Metal Complexes 39, DOI 10.1007/978-3-319-54161-7_8

investigated [3–5]. In the laboratory, recycling tests are very time-consuming and often inaccurate because of small catalyst losses or contact with air. The catalyst recycling in a continuously operated and closed miniplant is easily done and very secure. Long-term experiments of about a week or longer are of no problem [6].

In the following chapters, the construction and operation of miniplants will be described on different examples with renewables in which also carbon dioxide will be considered. The telomerisation of 1,3-butadiene with CO_2, glycerol and sucrose will be described in the present Chap. 8. Additionally, the co-oligomerisation of fatty compounds with ethene (Chap. 9), the hydroamination of the terpene myrcene (Chap. 10), and the hydroformylations (Chap. 11) of unsaturated oleochemicals are discussed.

8.1 Telomerisation of Butadiene with Carbon Dioxide

The telomerisation of 1,3-butadiene **1** with carbon dioxide **2** was first discovered by Inoue [7] and Musco [8] (see Chap. 5). The main product of this reaction is the δ-lactone 2-ethylidene-6-hepten-5-olid **3** (Fig. 8.1). Besides this target molecule also the γ-lactone **4,** the carboxylic acid **5,** and the ester **6** are formed. A further side product is the dimerisation product 1,3,7-octatriene **7**.

The optimum catalyst of this reaction is an in situ catalyst formed by the precursor palladium *bis*–(acetylacetonate) and, e.g., the bulky ligand tricyclohexylphosphine. Inspite of the low activity of CO_2, this telomerisation occurs already at very mild reaction conditions, for instance, at 80–90 °C and 10–40 bar. A typical reaction solvent is acetonitrile. In batch experiments, a conversion of butadiene of 48% and a high selectivity to the δ-lactone of 95% could be reached.

Considering these starting conditions, a first miniplant concept was designed (Fig. 8.2): The reaction occurs in a 3 L continuously stirred tank reactor (CSTR) with a residence time of 15 h. The condensed butadiene is pumped from a buffer

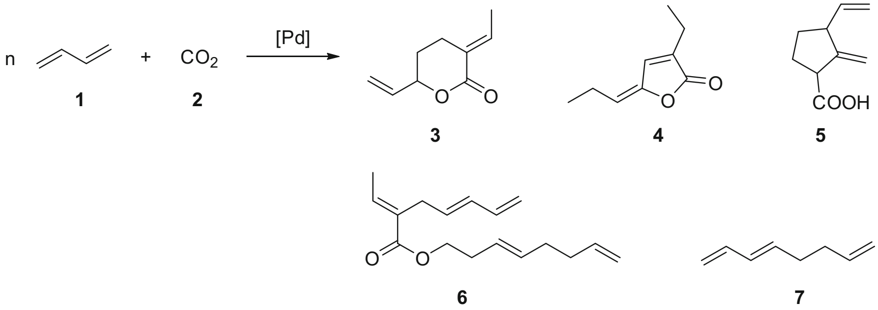

Fig. 8.1 Products of the telomerisation of 1,3-butadiene with carbon dioxide

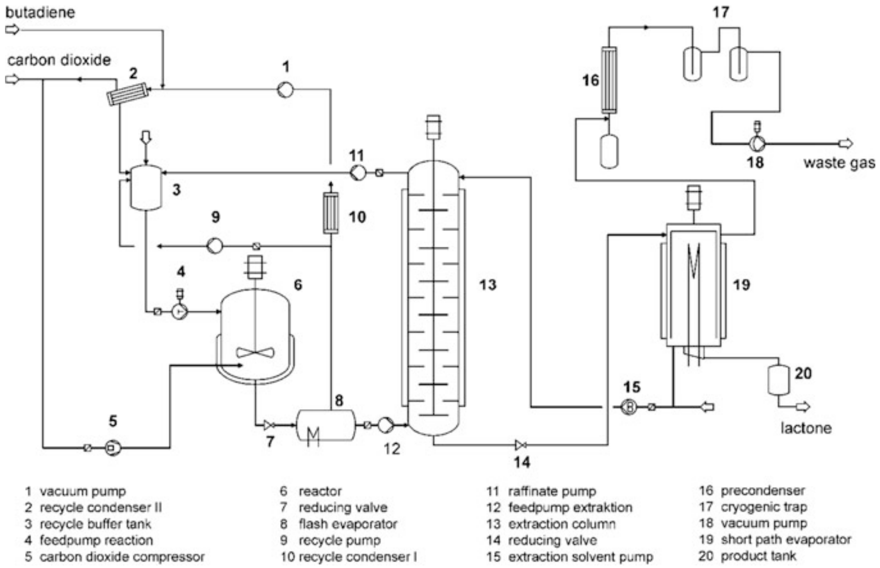

Fig. 8.2 Miniplant I for the telomerisation of 1,3-butadiene with carbon dioxide

tank into the reactor, and the carbon dioxide is pressed in via a compressor. The effluent of the reactor contains 20% of δ-lactone, but also unreacted butadiene, CO_2, acetonitrile, the side products, and the catalyst [9].

This mixture is then separated by flash evaporation in reduced pressure at temperatures below 100 °C yielding a vapour phase with carbon dioxide, butadiene, and acetonitrile (which can be recycled to the reactor) and a liquid phase consisting of more than 95% δ-lactone, side products, and catalyst. At first, a distillation of this product mixture was avoided because it was known that at higher temperatures and longer load periods the δ-lactone **3** converts into the non-wanted γ-lactone **4.** Thus, a smooth extraction step was developed: With 1,2,4-butanetriol, which has a clearly higher boiling point than the δ-lactone, the lactone could be extracted nearly completely from the mixture at a mild temperature of 60 °C. At lower temperatures, the viscosity of the triol is too high. In batch experiments, no additional reaction of the extractant solvent was observed. The raffinate phase of the extractor containing the higher boiling side products, and the catalyst was recycled to the reactor; the catalyst-free extract phase containing the triol, and the δ-lactone was separated by vacuum distillation in a short path evaporator with a short retention time and a heating medium temperature of 145 °C. Thus, a pure δ-lactone was isolated, and the triol was recycled back to the extractor.

These operations were carried out continuously in miniplant I for 24 h run-time. The non-reacted starting compounds, the solvent acetonitrile, the catalyst, and the high boiling side products were recycled continuously. Surprisingly, no accumulation of the side products occurred. Obviously, in the reactor, these side products are in a catalysed equilibrium with the δ-lactone so that no new side products are formed. Thus, in the miniplant I operated continuously for 24 h butadiene, and carbon dioxide seemed to react selectively only to the wanted δ-lactone.

However, in the operation of the miniplant for a running time of several days, a considerable decrease of the yield of the δ-lactone was observed. In addition, it was also realised that small amounts of the extractant 1,2,4-butanetriol occurred in the raffinate stream which accumulated in the reaction phase, thus slowly deactivating the catalyst.

The separation concept had to be changed, and a reconstructed miniplant II had to be installed [10–12]. The flow scheme of the slightly changed miniplant is show in Fig. 8.3.

In miniplant II, the extraction step was removed and instead the already existing short path evaporator was used to separate the catalyst from the product. However, this thermic separation is only possible at temperatures which do not destroy the catalyst. After careful optimisation of the separation conditions, the following steps were developed: The reaction mixture is first separated in the flash evaporator at 80 °C and 150 mbar. The remaining liquid phase, containing δ-lactone, side products, and catalyst, is then conducted to the short path evaporator where the δ-lactone is smoothly separated from the catalytic residue at 80 °C and 1.5 mbar. Using these conditions, miniplant II was operated for several days where the miniplant worked satisfying under steady-state conditions. The miniplant produced the δ-lactone in a constant amount of 8 g/h without catalyst deactivation or side product accumulation. In an industrial production of the δ-lactone, the very high vacuum generates relatively high costs which are only economic if the product is sufficiently valuable.

A certain disadvantage of the hitherto process is the fact that toxic acetonitrile is used as solvent. To avoid this handicap, other solvents were investigated, and it was found that cyclic carbonate solvents like ethylene, propylene, or butylene carbonate

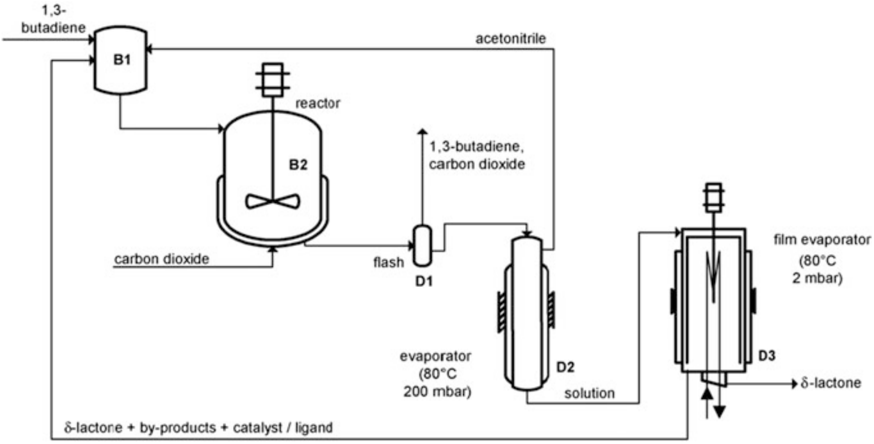

Fig. 8.3 Miniplant II for the telomerisation of 1,3-butadiene with carbon dioxide

are very attractive solvents in CO_2 telomerisation [11, 12]. Furthermore, cyclic carbonates with ester groups like glycerol carbonate propionate or butyrate could be tested successfully. These glycerol carbonates have the advantage that their boiling points are much higher than the boiling point of the δ-lactone. Thus, they are not separated in the flash evaporator but as high boilers in the short path evaporator.

8.2 Telomerisation of Butadiene with Glycerol

The telomerisation of butadiene with the trifunctional molecule glycerol yields a number of different products because in principle all three hydroxy functionalities of the glycerol—both primary and secondary ones—can react in the telomerisation reaction. Thus, unsaturated linear or branched mono-, di- and trioctadienylethers can be formed (Fig. 8.4). Of course also the butadiene-dimer, 1,3,7-octatriene can be formed as unwanted by-product.

Especially, the telomers which still obtain free hydroxy groups are of high industrial significance because they can easily be converted to anionic or non-ionic detergents, emulsifiers, or anti-foaming agents. However, if the telomerisation is carried out in a homogeneous phase, e.g. in isopropanol, only broad mixtures are formed which contain both non-reacted glycerol and a greater amount of the non-wanted tritelomers. Thus, the reaction performs better in an organic-aqueous biphasic system. The palladium catalyst is formed in situ from $Pd(acac)_2$ and the sodium salt of triphenyl-phosphine-trisulfonate (TPPTS). The palladium catalyst dissolves splendidly in the water phase in which also the glycerol is solved. The second phase is an organic phase, e.g. a solvent like toluene or the compressed liquid starting compound butadiene. By extensive mixing, sufficient butadiene solves in the water–glycerol–catalyst phase where the reactions take place. The first reaction step is the formation of the monooctadienylether of glycerol which dissolves relatively well in the organic phase so that no (or little) further reaction to the di- and tritelomers can occur. Thus, the biphasic telomerisation of butadiene with glycerol yields relatively selective the monotelomers and few amounts of the ditelomers. A slight disadvantage is the fact that in the presence of water also small amounts of the water telomer, the 2,7-octadienol, is formed (Fig. 8.5).

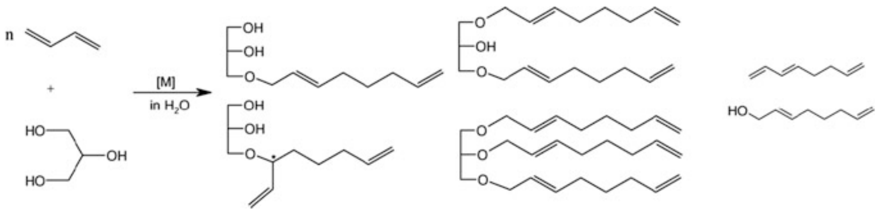

Fig. 8.4 Products of the telomerisation of butadiene with glycerol

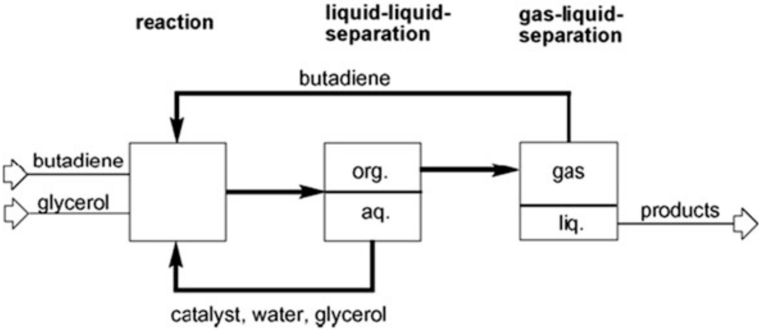

Fig. 8.5 Process scheme of the biphasic telomerisation of butadiene with glycerol

This liquid–liquid two-phase technique, which was already applied successfully in glycol telomerisation [13–16], is also very suitable for glycerol telomerisation [17]. As shown in Fig. 8.5, this technique has the great advantage that by a simple liquid–liquid-separation step the catalyst is separated from the products and can easily be recycled to the reactor. The organic product phase still contains some unreacted butadiene which can also be recycled via a subsequent gas–liquid separation step.

For this telomerisation, a continuously operated miniplant was constructed [18–20] (Fig. 8.6). Due to the application of stabilizing agents, such as phosphonium salts and radical scavengers to prevent the polymerisation fouling of butadiene, this process could be run for more than 250 h with constantly high yield of monotelomers and a low palladium leaching below 20 ppm. All recycling loops were closed, and a space-time yield of 20 kg m^{-3} h^{-1} was obtained.

8.3 Telomerisation of Butadiene with Sucrose

As already mentioned in the telomerisation chapter, the reactions with sugars as nucleophiles are very attractive. Monosaccharides like glucose, xylose, or arabinose were already tested, but also disaccharides like sucrose or even polysaccharides like starch have been used in telomerisation with butadiene or sometimes with isoprene or piperylene [20].

In the glycerol miniplant described above—after some minor modifications—also the telomerisation of butadiene and sucrose was tested in continuous operation [21]. With the same Pd/TPPTS catalyst, the liquid–liquid two-phase technique was used with a mixture of water and isopropanol as polar catalyst phase. A mixture of eight isomeric telomers was formed which proved all to be sucrose monooctadienyl ethers. Once again small amounts of 2,7-octadienol occurred as by-products. In this isopropanol–water mixture, the amount of palladium in the organic product phase was only 11 ppm. A great technical problem during the investigations was the

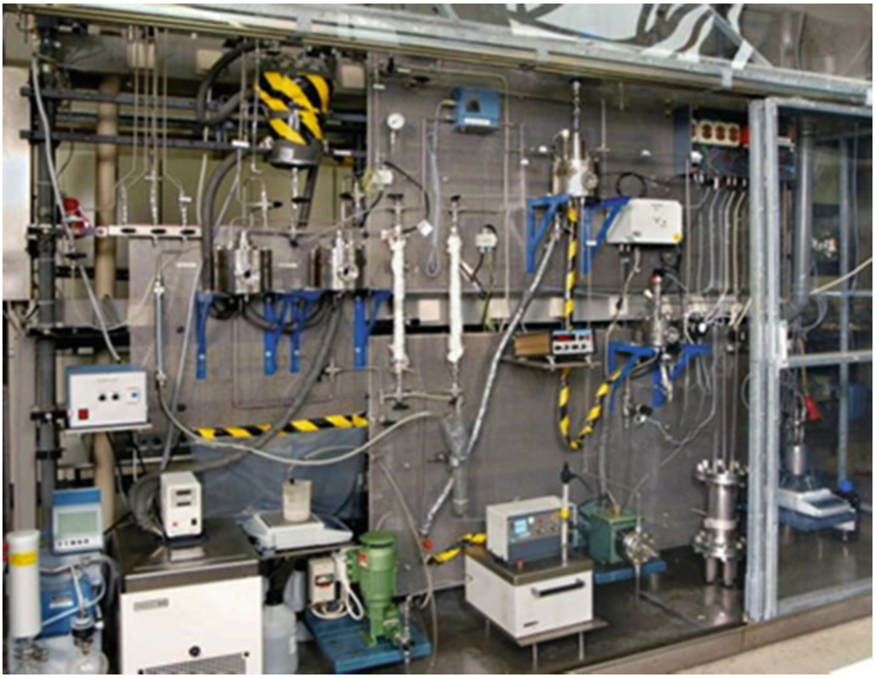

Fig. 8.6 Picture of the continuously operated miniplant for the telomerisation of butadiene with glycerol

dosage of the small amounts of the solid material sugar in the miniplant scale. To circumvent this problem, the nucleophile sucrose was fed into the plant as a highly concentrated aqueous sugar solution. However, using this technique, the water is little by little enriched in the reaction part of the miniplant, thus not allowing a really stationary operation. Like the well-known alkyl polyglucosides (APG), the sucrose monotelomers are of high interest for the detergent market.

References

1. Behr A, Ebbers W, Wiese N (2010) Chem Ing Techn 72:1157
2. Bahke P, Behr A, Górak A, Hoffmann A (2006) In: Deibele L, Dohrn R (eds) Miniplant-Technik in der Prozessindustrie, Chapt. 5.1. Wiley-VCH, Weinheim, pp 199–232
3. Behr A, Keim W (1987) Erdöl, Erdgas, Kohle 103:126–130
4. Behr A (1998) Chem Ing Techn 70:685–695
5. Behr A, Neubert P (2012) Applied homogeneous catalysis. Wiley-VCH, Weinheim
6. Behr A, Witte H, Zagajewski M (2012) Chem Ing Tech 84:694–703
7. Sasaki Y, Inoue Y, Hashimoto H (1976) J Chem Soc D 605–606
8. Musco A, Perego C, Tartiani V (1978) Inorg Chim Acta 28:147–148

9. Behr A, Heite M (2000) Chem Eng Technol 23:952–955
10. Behr A, Bahke P, Becker M (2004) Chem Ing Tech 76:1828–1832
11. Behr A, Becker M (2006) Dalton Trans 4607–4613
12. Behr A, Bahke P, Klinger B, Becker M (2007) J Mol Catal A: Chem 267:149–156
13. Behr A, Urschey M (2003) Adv Synth Catal 345:1242–1246
14. Behr A, Urschey M (2003) J Mol Catal A: Chem 197:101–113
15. Behr A, Urschey M, Brehme VA (2003) Green Chem 5:198–204
16. Behr A, Seuster J (2005) In: Cornils B et al Multiphase homogeneous catalysis. Wiley-VCH, Weinheim, pp 114–122
17. Behr A, Leschinski J, Awungacha C, Simic S, Knoth T (2009) ChemSusChem 2:71–76
18. Behr A, Leschinski J, Prinz A, Stoffers M (2009) Chem Eng Process 48:1140–1145
19. Behr A, Leschinski J (2009) Green Chem 11:609–613
20. Behr A, Becker M, Beckmann T, Johnen L, Leschinski J, Reyer S (2009) Angew Chem Int Ed 48:3598–3614
21. Schlussbericht Entwicklung, Aufbau und Betrieb einer Miniplant-Anlage zur kontinuierlichen Herstellung von Saccharosetelomeren (“Sacchasrosetelomerisation”), 2014, BMBF-Förderprogramm TU Dortmund/Südzucker AG