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Hydrogenation

Propane-1,2-diols from Dilactides, Oligolactides, or Poly-L-lactic Acid (PLLA): From Plastic Waste to Chiral Bulk Chemicals

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In memory of Karsten Krohn

Abstract: The preparation of racemic or enantioenriched propane-1,2-diol from dilactides, oligolactides, or poly-L-lactic acid (PLLA) is described. The transformation is carried out as tandem reactions in MeOH, covering hydrolysis and subsequent hydrogenation by using copper chromite as a catalyst. The starting material present undesired side products of the PLLA synthesis or PLLA waste.

The application of biodegradable polymers in packaging or one-way cutlery is one of the most important measurements to reduce the vast amounts of waste worldwide. Poly-L-lactic acid (PLLA) derived from natural L-(+)-(*S*)-lactic acid is one of most promising material for such purpose.[1] It is assumed that in near-future PLLA will have a similar potential like polyethylene terephthalate (PET), but with different field of application.[1g] Unfortunately to date, the production costs are relatively high in comparison to their petrochemically based analogues.

PLLAs are usually produced by the ring-opening polymerization of (*S*,*S*)-dilactide.[1g] (*S*,*S*)-Dilactide is available by thermal metal-catalyzed dimerization of (*S*)-lactic acid; the latter can be derived by fermentation of corn, potato, or even garbage.[1g, 2, 3] During the lactonization besides the desired (*S*,*S*)-dilactide, also considerable amounts of *meso*-(*S*,*R*)-dilactide are formed, which seriously affects the overall economy of the manufacturing of PLLA on a large scale. *meso*-Dilactide impacts the properties of the resulting PLLA if incorporated and thus has to be removed.[1 g] Methods to use the *meso*-compound for the production of other valuable chemicals are therefore of high interest.

Since few years, we focus our research on the improvement of the cost efficiency of the industrial PLLA manufacture.[4] Reducing costs of the PLLA production, avoidance or beneficial utilization of by-products, as well as an efficient recycling of PLLA, are challenging goals within this framework.[1g, 5]

The synthesis of propane-1,2-diol (propylene glycol) from undesired lactides or PLLA waste could solve two problems at once. First, it can greatly diminish the overall costs of PLLA production. On the other hand, it offers an attractive and scalable approach to propane-1,2-diol based on renewable resources. Commonly used propane-1,2-diol is produced industrially from propylene through propylene oxide (HPPO process),[6] and therefore it is crude oil derived. The annual production is close to 1 Mio tons.[7] The main part is used for the manufacture of polyesters or polyurethanes. Alternatively, it may serve for the production of propylene carbonate, which is a valuable and environmental friendly solvent for several applications.[8] The production of propane-1,2-diol starting from lactic acid derivatives would offer the possibility to change the feedstock basis. In addition, since the generally applied enzymatic venues to lactic acid produce enantiopure compounds, subsequent transformations may afford enantiopure propane-1,2-diol with new sale prospects at the market than its racemic mixture.

Herein, we report a simple one-pot protocol for the preparation of racemic or almost enantiomerically pure (*S*)-propane-1,2-diol starting from different lactides, which give the diol in excellent yield.

Alcoholysis hydrogenation of di- and oligolactides

The ring-opening hydrogenation of dilactides is an interesting challenge for the synthesis of propane-1,2-diol. To the best of our knowledge, this tandem reaction has not been described in the literature to date.[9] In contrast, the hydrogenation of none-cyclic lactic acid esters, such as alkyl lactates, has been already established.[10, 3b] The reaction requires normally high temperatures and hydrogen pressures.[10a, b] For the reduction, alcohols are commonly applied as solvent.

Our initial screening experiments revealed that dilactides are resistant to hydrogenation conditions at low temperatures up to 100 °C by using heterogeneous ruthenium catalysts, such as

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5% Ru on charcoal, 5% Ru on Al_2O_3, and 5% Ru with 0.25% Pd on charcoal. Noteworthy, only transesterification took place in alcoholic medium. The rates of the ring cleavage of the lactide and the following alcoholysis were mainly dependent on the nature of the catalyst support. Thus, ruthenium on aluminium oxide promoted the reaction much more efficient than ruthenium on charcoal. With the former, a ratio of methyl lactoyl lactate to methyl lactate of 1:2 was obtained, whereas with the latter—a ratio of 10:1 was obtained after 4 h at 90 °C. These observations inspired us to find reaction conditions, in which the alcoholysis of dilactides proceeds fast giving lactates, which are immediately subjected to the hydrogenation.

Indeed, preliminary experiments with copper chromite (Cu/Cr) and barium-promoted copper chromite (Cu/Cr/Ba)[10a,11,12] as catalysts showed that *rac*-dilactide can be converted into propane-1,2-diol at 150 °C and 150 bar in methanol with excellent chemoselectivity and in high yield (Table 1, runs 1–4). Remarkably, products of deoxygenation were not observed at all. The barium-promoted copper chromite catalyst was superior in terms of separation by centrifugation.

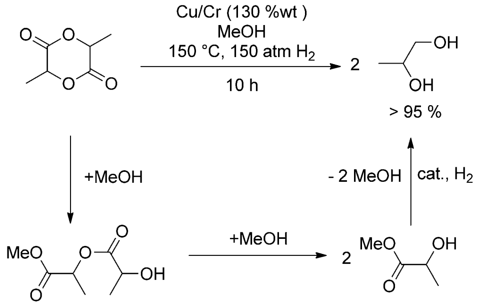
Table 1. Alcoholysis hydrogenation of stereoisomeric dilactides.[a]

Run	Dilactide	Load [g]	*t* [h]	*T* [°C]	Catalyst	Yield[b] [%]
1	*rac*	0.15	5	125	Cu/Cr (33 wt%)	40
2	*rac*	0.15	5	150	Cu/Cr (33 wt%)	70
3	*rac*	0.15	5	150	Cu/Cr (133 wt%)	99
4	*rac*	0.15	5	150	Cu/Cr/Ba (130 wt%)	99
5[c]	*rac*	1.0	5	90	Cu/Cr/Ba (130 wt%)	19
6	*rac*	1.0	10	99	Cu/Cr/Ba (133 wt%)	99
7[d]	*rac*	1.0	10	99	Cu/Cr/Ba (133 wt%)	99
8	*rac*	0.5	15	150	Cu/Cr/Ba (130 wt%)	99
9	*rac*	1.0	15	150	Cu/Cr/Ba (130 wt%)	99
10	(*S*,*S*)	1.0	15	150	Cu/Cr/Ba (130 wt%)	99
11	*meso*	1.0	15	150	Cu/Cr/Ba (130 wt%)	99

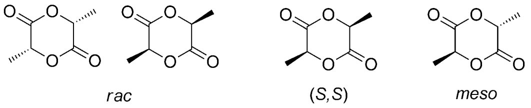
[a] Reaction conditions: 150 bar H_2, 5 mL MeOH. [b] Yield based on GC. [c] 90 bar H_2. [d] Recycled catalyst from run 6 was used.

In turn, the reaction was optimized. It was found that up to 0.2 g *rac*-dilactide (1.4 mmol) per 1 mL of methanol can be converted into propane-1,2-diol (runs 4, 8, 9). The transformation below 100 °C was slow (run 5). It should be noted that methanol acts as a solvent as well as a reagent, but it was not consumed during the transformation. In all experiments, full conversion of dilactide was achieved. Methyl lactoyl lactate and methyl lactates were the only by-products observed in those cases, in which the reaction was not complete (Scheme 1). The observation of these esters gave proof that both are intermediates in the transformation to propane-1,2-diol. Under the employed reaction conditions, all stereoisomers of dilactide could be converted into the final product (Scheme 2).

Recycling of catalyst was possible without loss of activity (runs 6–7). Equal yields of propan-1,2-diol were obtained in the reaction of racemic dilactide, (*S*,*S*)-, and *meso*-dilactides under the same reaction conditions (runs 9–11). In the presence of water or free lactic acid, the catalyst was deactivated and metallic copper precipitated on the walls of the autoclave.



Scheme 1. Alcoholysis hydrogenation of *rac*-dilactide in methanol.



Scheme 2. Diastereomeric lactides used as substrates.

The reaction in ethanol proceeded much slower. Thus, full conversion of 0.5 g *rac*-dilactide (3.5 mmol) in 5 mL ethanol was observed only after 15 h. At higher concentrations of dilactide, complete conversion was not reached within this time.

Unfortunately, propane-1,2-diol was not suited for the direct determination of the enantiomeric-excess (*ee*) values by GC at chiral columns. Therefore, it was converted into the corresponding bis(phenylurethane) derivative and analyzed by HPLC analysis on Chiralcel OD-H. Similarly useful revealed the formation of the bis(trifluoroacetate) derivative, which was subjected to GC analysis on a Lipodex E column.[13]

Next, the temperature dependency of the stereoselectivity in the hydrogenation of (*S*,*S*)-dilactide was studied. It was found that the *ee* of the formed propane-1,2-diol is strongly affected by the reaction temperature (Table 2). At 150 °C, the hydrogenation procedure gave exclusively racemic product. A decrease of the reaction temperature to 125 °C gave (*S*)-propane-1,2-diol with 74% *ee*. At 100 °C, almost no epimerization took place, and (*S*)-propane-1,2-diol was obtained with 98% *ee*. Under these conditions, the rate of the reaction was lowered.

After that, the hydrogenation of hexalactide was studied to broaden the scope of the reaction. The substrate was synthesized by using a modified procedure of Chisholm et al. from *rac*-dilactide.[14] Thus, a mixture of stereoisomeric hexalactides was obtained from the reaction of sodium tetraphenylborate-hexalactide with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine. The mixture was azeotropically dried with benzene.

Table 2. Alcoholysis hydrogenation of (*S*,*S*)-dilactide.[a]

Run	*t* [h]	*T* [°C]	Yield[b] [%]	*ee*[c] [%]
1	12	150	100 (82)	0
2	12	125	90	74
3	15	100	80	98

[a] Reaction conditions: 5 mL MeOH, 0.5 g (*S*,*S*)-dilactide, 133 wt% Cu/Cr/Ba, 150 bar H_2. [b] Yield based on GC (isolated yield in parentheses). [c] Determined by GC at Lipodex E.

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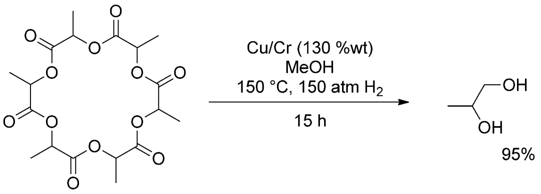
We were pleased to see that in the subsequent alcoholysis hydrogenation under the conditions described above also hexalactide reacted to give exclusively propane-1,2-diol in an excellent yield (Scheme 3).



Scheme 3. Alcoholysis hydrogenation of hexalactide.

Alcoholysis hydrogenation of poly-L-lactic acid polymers (PLLA)

The results discussed above gave us hope that not only dimers and oligomers, but also PLLA can be successfully subjected to our tandem-reaction protocol. This transformation attracts particular attention by employment of waste of PLLA.

The recycling of PLLA was intensively investigated over the past decade. Different procedures, such as hydrolysis with water or aqueous solutions,[15,16] alcoholysis with alcohols and their mixtures,[17–19] reaction with amines,[20] as well as thermal degradation,[21–24] are known. The transformation into propane-1,2-diol has not been studied to date.

Our experiments showed that the hydrogenation procedure coupled with prior alcoholysis proceeds smoothly also with polymeric lactides with a molecular weight >15000 Da. As has been already noted with dilactides, the *ee* of the resulting (*S*)-propane-1,2-diol is dependent on the hydrogenation temperature (Table 3). At 100 °C, the enantioenriched product was obtained with 90% *ee*.

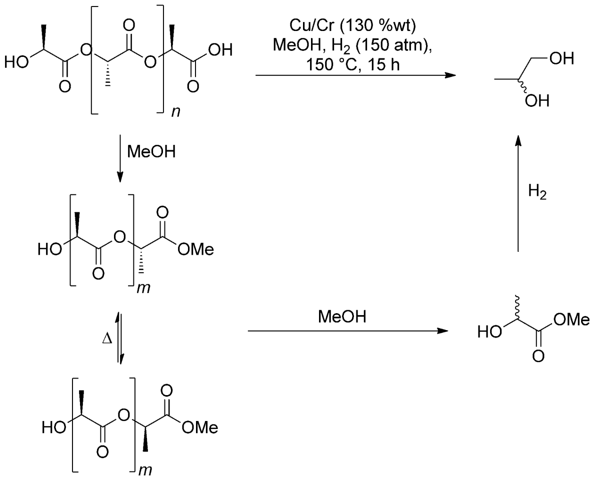
Table 3. Stereoselectivity of the alcoholysis hydrogenation of PLLA.[a]

Run	*t* [h]	*T* [°C]	Yield[b] [%]	*ee*[c] [%]
1	15	100	50	90
2	15	125	99	40
3	12	150	99 (88)	0

[a] Reaction conditions: 5 mL MeOH, 0.15 g PLLA, Cu/Cr/Ba (133 wt%), 150 bar H_2. [b] Yield based on GC (isolated yield in parentheses). [c] Determined by GC at Lipodex E.

It seems that at elevated temperature, the epimerization occurred mostly with lactoyl lactates or longer-chain oligomers of lactic acid. Enantiomerically pure propane-1,2-diol turned out to be stable under these conditions. Because the cleavage of PLLA with methanol proceeded slower than the alcoholysis of dilactides with the former substrate, a lowered enantioselectivity in the final product was noted (Scheme 4).

In conclusion, we have developed a new and highly efficient protocol for the transformation of di-, oligo-, or polylactides (PLLA) into propane-1,2-diol based on a tandem reaction covering alcoholysis and subsequent hydrogenation. Under optimized reaction conditions and by using enantiomerically pure lactides, the reaction gives (*S*)-propane-1,2-diol with high enantioselectivity. The new transformation allows the use of lactic acid derivatives, which are commonly produced from renewable resources for the production of the bulk chemical propane-1,2-diol and, therefore, it is a contribution to sustainable chemistry.



Scheme 4. Hydrogenation of PLLA and epimerization as side reaction.

Experimental Section

All reagents, unless otherwise mentioned, were purchased from commercial sources and used without additional purification. Solvents were dried and freshly distilled under argon before use. Copper chromite was purchased from Aldrich. Barium-promoted copper chromite was purchased from STREM Chemicals and was finely powdered before use. For the determination of the enantiomeric ratio, GC was used at columns with chiral stationary phases (Lipodex E column) from Macherey–Nagel GmbH.

Alcoholysis hydrogenation of *rac*-dilactide

DL-Dilactide (1.00 g, 6.9 mmol) barium-promoted copper chromite (1.33 g, 133 wt%) and absolute MeOH (5 mL) were placed in autoclave (10 mL). The autoclave was rinsed three times with H_2, and then a pressure of 150 bar H_2 was pressed. The reaction mixture was stirred 12 h at 150 °C. The H_2 pressure was kept constant between 148 and 153 bars. The autoclave was cooled to RT and ventilated. The reaction mixture was diluted with MeOH (5 mL), and the catalyst was removed by centrifugation (15 min, 4500 rpm). The resulted reaction mixture was concentrated under reduced pressure. The blue-colored crude product (1.03 g) consisted of propane-1,2-diol with about 5% MeOH (^{13}C NMR spectrum). The pure product was obtained as colorless liquid (0.88 g, 82%) by distillation at 101–102 °C and 8 mbar.

Preparation of hexalactide

To a suspension of $[(CH_3CHC(O)O)_6]NaBPh_4$ (2.30 g, 3.10 mmol) prepared from *rac*-lactide[14] in CH_3CN (20 mL) was added TMEDA (3.0 mL, 20 mmol), and the reaction mixture was heated at reflux at 90 °C for 20 h. After filtration, the filtrate was evaporated to give a brown sticky solid. The solid was extracted with $CHCl_3$ (2×

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15 mL). The organic phases were combined and concentrated under reduced pressure. The brown oil was passed through a SiO_2 plug by using $CHCl_3$ as eluent to give 0.40 g of a waxy solid. The material was passed through a 1.0×17 cm SiO_2 column over $CHCl_3$, and the collected fractions were monitored by GC at a HP5 column. The product (0.2 g) was dried azeotropically with benzene.

Alcoholysis hydrogenation of hexalactide

Hexalactide (0.20 g, 0.5 mmol), barium-promoted copper chromite (0.26 g, 133 wt%), and absolute MeOH (5 mL) were placed in a autoclave (10 mL). The alcoholysis hydrogenation was carried out as was described for *rac*-dilactide. The reaction mixture was diluted with MeOH (5 mL), and the catalyst was removed by centrifugation (40 min, 4500 rpm). The resulted reaction mixture was concentrated under reduced pressure. The product was obtained as colorless liquid (0.15 g, 72%).

Alcoholysis hydrogenation of PLLA

A grinded one-way glass made from PLLA (0.50 g), barium-promoted copper chromite (0.67 g, 133 wt%) and absolute MeOH (5 mL) were placed in autoclave (10 mL). The alcoholysis hydrogenation was carried out as described for *rac*-dilactide. The reaction mixture was diluted with MeOH (5 mL), and the catalyst was removed by centrifugation (40 min, 4500 rpm). The resulted reaction mixture was concentrated under reduced pressure. The product was obtained as colorless liquid (0.46 g, 88%).

Derivatization of propane-1,2-diol

Trifluoroacetic acid anhydride (0.75 g, 3.6 mmol) was added slowly at 0 °C to propane-1,2-diol (0.1 g, 1.3 mmol) from the hydrogenation experiments. The reaction mixture was stirred 60 min at RT. Then it was diluted with dichloromethane (5 mL) and washed twice with aqueous $NaHCO_3$ (2×10 m). The organic phase was separated und dried over $MgSO_4$. The solvent was removed under reduced pressure. The product was used for the determination of *ee* values.

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Keywords: hydrogenation · lactides · propane-1,2-diol · synthetic methods · tandem reactions

[1] a) J. W. Leenslag, A. Pennings, *J. Makromol. Chem.* **1987**, *188*, 1809–1814; b) A. Kowalski, A. Duda, S. Penczek, *Macromolecules* **1998**, *31*, 2114–2122; c) H. R. Kricheldorf, I. Kreiser-Saunders, A. Stricker, *Macromolecules* **2000**, *33*, 702–709; d) K. M. Stridsberg, M. Ryner, A. C. Albertsson, *Adv. Polym. Sci.* **2002**, *157*, 41–65; e) A. P. Gupta, V. Kumar, *Eur. Polym. Mater.* **2007**, *43*, 4053–4074; f) M. Baśko, P. Kubisa, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 2650–2658; g) *Poly(Lactic Acid), Synthesis Structures, Properties, Processing and Application* (Eds.: R. Auras, L.-T. Lim, S. E. M. Selke, H. Tsuji), Wiley, Hoboken, **2010**.

[2] a) Y. Oda, K. Saito, H. Yamauchi, M. Mori, *Curr. Microbiol.* **2002**, *45*, 1–4; b) L. P. Huang, B. Jin, P. Lant, *Bioprocess Biosyst. Eng.* **2005**, *27*, 229–238.

[3] a) S. Inkinen, M. Hakkarainen, A.-C. Albertsson, A. Sodergard, *Biomacromolecules* **2011**, *12*, 523–532; b) M. Dusselier, P. Van Wouwe, A. Dewaele, E. Makshina, B. F. Sels, *Energy Environ. Sci.* **2013**, *6*, 1415–1442; c) No inventor (to E. I. Du Pont de Nemours and Company), GB 1007347, 1965; d) M. Aigner, W. Dersch (to Boehringer Ingelheim Int.), EP 264926, 1992; e) M. Mueller, (to Boehringer Ingelheim Int.) EP 261572, 1988.

[4] a) I. A. Shuklov, N. V. Dubrovina, J. Schulze, W. Tietz, K. Kühlein, A. Börner, *Tetrahedron Lett.* **2012**, *53*, 6326–6328; b) I. A. Shuklov, N. V. Dubrovina, J. Schulze, W. Tietz, K. Kühlein, A. Börner, *ARKIVOC (Gainesville, FL, U.S.)* **2012**, 66–75; c) I. A. Shuklov, H. Jiao, J. Schulze, W. Tietz, K. Kühlein, A. Börner, *Tetrahedron Lett.* **2011**, *52*, 1027–1030.

[5] a) M. S. Holm, S. Saravanamurugan, E. Taarning, *Science* **2010**, *328*, 602–605; b) F. de Clippel, *J. Am. Chem. Soc.* **2012**, *134*, 10089–10101; c) C. A. Ramirez-Lopez, *Ind. Eng. Chem. Res.* **2010**, *49*, 6270; d) J. Ecker, M. Schaffenberger, W. Koschuh, M. Mandl, H. G. Böchzelt, H. Schnitzer, M. Harasek, H. Steinmüller, *Sep. Purif. Technol.* **2012**, *96*, 237–247; e) H. Danner, L. Madzingaidzo, M. Holzer, L. Mayrhuber, R. Braun, *Bioresour. Technol.* **2000**, *75*, 181–187.

[6] See, for example: http://www.chemistryinnovation.co.uk/stroadmap/roadmap.asp-id=445.htm; http://www.uhde-ftp.de/press/pressshow.en.epl?stamp=150000046.

[7] C. J. Sullivan, *Propanediols* in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2005**, doi:10.1002/14356007.a22_163.

[8] B. Schäffner, F. Schäffner, S. Verevkin, A. Börner, *Chem. Rev.* **2010**, *110*, 4551–4581.

[9] Two procedures of hydrogenation of lactides were reported independently first by us and then by Milstein and co-workers in **2011**: a) W. Tietz, J. Schulze, A. Börner, I. Shuklov, K. Kühlein (to Thyssen Krupp Uhde GmbH) DE102011107959, 2013; b) E. Balaraman, E. Fogler, D. Milstein, *Chem. Commun.* **2012**, *48*, 1111–1113.

[10] a) H. Adkins, H. R. Billica, *J. Am. Chem. Soc.* **1948**, *70*, 3121–3125; b) G.-Y. Fan, Y. Zhang, Y.-F. Zhou, R.-X. Li, H. Chen, X.-J. Li, *Chem. Lett.* **2008**, *37*, 852–853; c) D. J. Moody, M. Härröd, R. Fieldhouse (to Avecia Ltd.), WO 2005023737, 2005; d) G. Luo, S. Yan, M. Qiao, K. Fan, *Appl. Catal. A* **2007**, *332*, 79–88; e) M. Studer, S. Burkhardt, H.-U. Blaser, *Adv. Synth. Catal.* **2001**, *343*, 802–808; f) W. Kuriyama, T. Matsumoto, O. Ogata, Y. Ino, K. Aoki, S. Tanaka, K. Ishida, T. Kobayashi, N. Sayo, T. Saito, *Org. Process Res. Dev.* **2012**, *16*, 166–171.

[11] For a comparison of copper/chromium catalysts, see: a) H. Adkins, E. E. Burgoyne, H. J. Schneider, *J. Am. Chem. Soc.* **1950**, *72*, 2626–2629; b) F. E. Brown, R. E. Menzel, M. M. Stewart, P. A. Lefrancois, *J. Am. Chem. Soc.* **1950**, *72*, 5602–5605.

[12] D. E. Cladingboel, *Copper Chromite* in *Encyclopedia of Reagents for Organic Synthesis*, Wiley, Hoboken, **2001**, doi:10.1002/047084289X.rc22.

[13] For the preparation of the bis(phenylurethane)derivative, see: P. A. Levene, A. Walti, *J. Biol. Chem.* **1926**, *68*, 415–424.

[14] M. H. Chisholm, J. C. Gallucci, H. Yin, *Dalton Trans.* **2007**, 4811–4821.

[15] L. D. Brake (to Du Pont De Nemours and Company), US5264626, 1993.

[16] H. Tsuji in *Poly(Lactic Acid): Synthesis, Structures, Properties, Processing, and Applications.* (Eds.: R- Auras, L.-T. Lim, S. E. M. Selke, H. Tsuji), John Wiley & Sons, Hoboken, **2010**, pp. 345–381.

[17] K. Hirao, Y. Nakatsuchi, H. Ohara, *Polym. Degrad. Stab.* **2010**, *95*, 925–928.

[18] L. D. Brake (to Du Pont De Nemours and Company), US5264617, 1993.

[19] P. Coszach, J. Willocq (to Galactic S. A.), WO 2011/029648, 2011.

[20] L. D. Brake (E. I. Du Pont De Nemours and Company), US 5268507, 1993.

[21] H. Nishida, Y. Fan, Y. Shirai (to Kyushu Institue of Technolgy, Kitakyushu for the Foundation for the Advancement of Indus, Kinki University), US20080004454, 2008.

[22] M. Hiroshi, M. Yutaka, Y. Koji (to Kobe Steel Ltd.), JP 11106554, 1999.

[23] H. Nishida, Y. Fan, Y. Shirai (to Japan) WO 2003/091238, 2003.

[24] H. Ohara, T. Okamato (Shimadzu Corp.), DE 19637404, 1997.

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