DOI: 10.1002/adsc.201000229

One-Step Surface Decoration of Poly(propyleneimines) (PPIs) with the Glyceryl Moiety: New Way for Recycling Homogeneous Dendrimer-Based Catalysts

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Received: March 24, 2010; Revised: June 28, 2010; Published online: August 16, 2010

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201000229.

Abstract: First to fifth generations of poly(propyleneimines) (PPIs) were reacted with glycerol carbonate yielding a new family of glycerol-decorated PPIs (GD-PPI). Owing to the presence of glyceryl units surrounding the PPI core, the high generation GD-PPI-5 can be successfully immobilized in a glycerol phase, thus offering a convenient route for possible utilization as a recyclable homogeneous catalyst. In this context, we show here that GD-PPI-5 can be used as a basic catalyst in the ring opening of epoxides with carboxylic acids in glycerol. The high affinity of GD-PPI-5 for the glycerol phase allowed us to (i) selectively extract the reaction products from the glycerol/GD-PPI-5 mixture and (ii) recycle the GD-PPI-5 catalyst. More generally, this work offers new tools for the convenient recycling of valuable but expensive dendrimers.

Keywords: catalyst immobilization; dendrimers; glycerol carbonate; glycerol-decorated dendrimers; green solvent

The recovery of homogeneous catalysts represents a very important issue in academia and in industry. To date many strategies have been reported such as the covalent grafting of homogeneous catalysts on a solid support,[1] their non-covalent immobilization[2] and their encapsulation within organic, inorganic or hybrid organic-inorganic polymers.[3] More recently, immobilization of homogeneous catalysts in a liquid phase has emerged as a feasible approach. In this context, ionic liquids,[4] polyethylene glycol[5] and fluorous solvents[6] have been widely investigated. Although fascinating works have been reported, these solvents have shortcomings such as high cost or toxicity. Within the framework of green chemistry, the utilization of water as a liquid phase for homogeneous catalyst immobilization has received considerable interest and elegant works have already emerged in the literature.[7]

Recently, we and others have reported that glycerol presents close similarities with water.[8] Indeed, like water, glycerol is naturally available, cheap and can be used as an environmentally friendly solvent for catalysis and organic chemistry. Like water, glycerol is poorly miscible with most of the organic solvents allowing a convenient extraction of the reaction products. Interestingly, glycerol is able to dissolve more hydrophobic substrates than water, thus offering a good means for the immobilization of a wider range of homogeneous catalysts. For an efficient immobilization in glycerol, the homogenous catalyst has to meet different criteria such as (i) have a high polarity in order to ensure a strong interaction with the glycerol phase and (ii) have a chemical inertia towards glycerol. In this context, dendrimers represents an attractive class of homogeneous catalyst for our purpose.[9] Indeed, despite promising catalytic properties, the high prices of dendrimers represent today the main

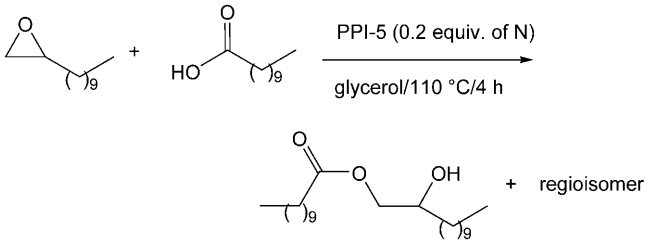
limitation for their wide utilization in industry and academia. Therefore, the search for innovative concepts that are capable of recycling this valuable but expensive homogeneous catalyst is highly worthwhile.

Among dendrimers, PPIs are of prime importance. Owing to their high polarity, PPIs are soluble in glycerol while the presence of weakly basic amino groups, which are unable to deprotonate glycerol, may act as basic catalytic sites. Here, we wish to report that the decoration of PPIs with glycerol moieties allowed their convenient immobilization in glycerol, thus offering a promising tool for (i) conveniently separating the reaction products from the glycerol/dendrimers catalytic phase and (ii) allowing the recycling of these glycerol-decorated PPIs (GD-PPI). In particular, we showed that there exists a close relationship between the generation of the GD-PPIs and their immobilization in the glycerol phase.

In a first set of experiments, we investigated the base-catalyzed ring opening of 1,2-epoxydodecane with dodecanoic acid in glycerol. For the above stated reasons, the fifth generation PPI-5 was first tested as a homogeneous catalyst. In a typical procedure, an equimolar mixture of 1,2-epoxydodecane and dodecanoic acid (1 mmol) was heated in 4 mL of glycerol at 110 °C and in the presence of 0.2 equiv. (based on the amount of nitrogen) of PPI-5. As summarized in the Table 1, PPI-5 was able to catalyze the ring opening of 1,2-epoxydodecane with dodecanoic acid in glycerol leading to a 69% yield of the desired esters after 4 h of reaction. The selectivity to the desired ester was not exclusive (75%) due to (i) the thermal degradation of the 1,2-epoxydodecane and (ii) the probable ring opening of the 1,2-epoxydodecane by the amino groups of the PPI-5.

At the end of the reaction, the products were easily recovered from the glycerol phase by liquid-liquid phase extraction with ethyl acetate.[10] Although the PPI-5 is highly polar, PPI-5 was unfortunately co-extracted with the reaction products. Therefore, during the recycling experiments, a significant drop in yield was observed and only a 21% yield of ester was obtained after the 4th catalytic run (Table 1).

Table 1. Ring opening of 1,2-epoxydodecane with dodecanoic acid catalyzed by PPI-5 in glycerol.



Entry	Catalytic cycle[a]	Epoxide conversion [%]	Isolated yield [%]
1	1	92	69
2	2	69	45
3	3	48	29
4	4	41	21

[a] All reactions were stopped after 4 h.

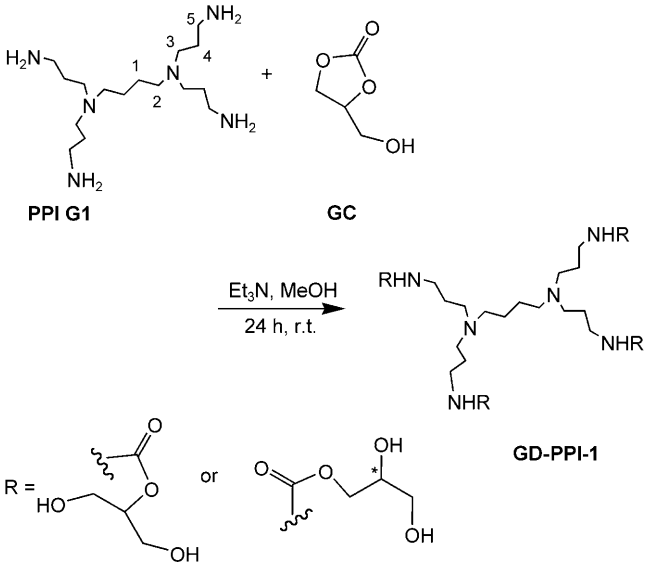
In order to circumvent this issue and to assure a better immobilization of PPI in the glycerol phase, we decided to decorate the PPIs with glycerol moieties. As we had functionalized P- or Si-based dendrimers with pentoses or pentoses derivatives[11] we attempted the functionalization of PPI dendrimers with glycerol units using glycerol carbonate as an organic building block. In the existing literature, it has been clearly established that primary amines readily reacted with glycerol carbonate to generate a glyceryl carbamate moiety.[12] In particular, this strategy is a safe and selective way to introduce a glyceryl unit onto a polymer backbone. Inspired by these works, different generations of GD-PPIs were prepared by reaction of PPIs with glycerol carbonate.

The first generation GD-PPI-1 was obtained by reaction of the terminal secondary amines of a first generation PPI (named PPI-1) with glycerol carbonate (Table 2). In a mixture THF/DMF, no reaction occurs due to the insolubility of the starting dendrimer (PPI-1) in such a mixture of solvents (Table 2, entry 1). Thus, we chose MeOH as solvent in which both the PPI-1 and the glycerol carbonate are highly soluble. The reaction of PPI-1 with one equivalent of glycerol carbonate (with respect to the primary amines of PPI-1) in MeOH led to 85% conversion of glycerol carbonate within 24 h (Table 2, entry 2). Note that the reaction proceeds here at room temperature illustrating the high reactivity of glycerol carbonate. When the amount of glycerol carbonate was slightly increased from 1.0 to 1.1 equiv., the conversion was increased up to 95% (Table 2, entry 3).

The reaction of PPI-1 with glycerol carbonate was clearly evidenced by ^{1}H NMR especially focussing on the chemical shift of the protons H-5 corresponding to the $-CH_2-NH_2$ group (2.7 ppm for PPI-1 and 3.14 ppm for PPI-GD1, see Experimental Section). While ^{1}H NMR confirmed the formation of GD-PPI-1 with a glycerol carbonate conversion of 95%, mass spectrometry (MS-MS analysis) revealed the non-negligible presence of a secondary product corresponding to the grafting of only three glyceryl units on the PPI-1. The purification of GD-PPI-1 was performed by solubilizing the crude mixture in a minimum of MeOH. To our delight, upon addition of pentane/ethyl acetate (2/1), the GD-PPI-1 precipitated as a pure product. After this purification step, the GD-PPI-1 was isolated with 78% yield.

Proceeding on the same lines, higher generations of GD-PPIs were prepared (Table 3). Using the same conditions as those described above for GD-PPI-1,

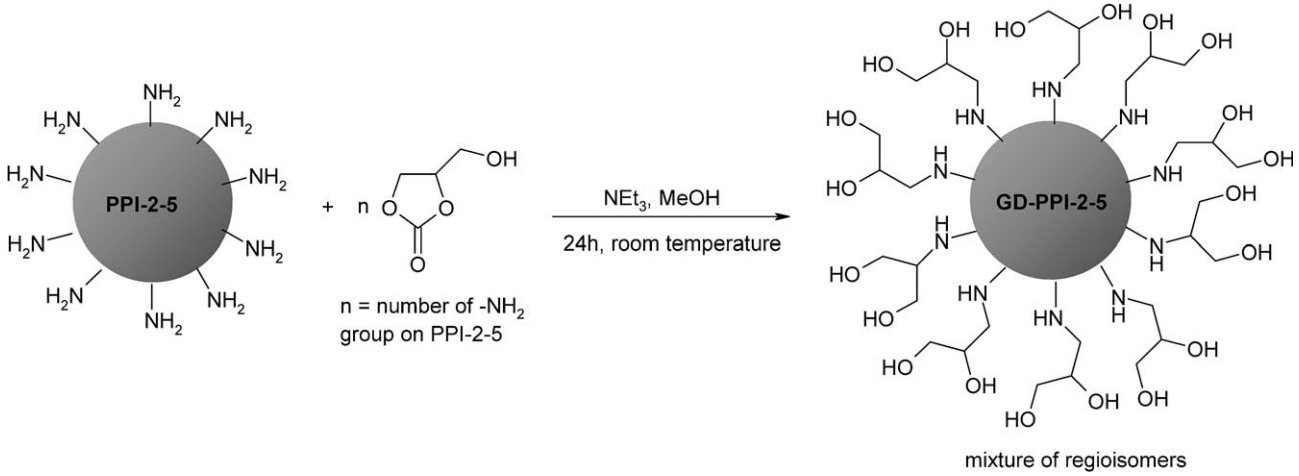
Table 2. Reaction conditions for the synthesis of GD-PPI-1.



Entry	Equiv. glycerol carbonate[a]	Solvent	Time [h]	Conv. [%]
1	1.1	THF/DMF	96	0
2	1.0	MeOH	24	85
4	1.1	MeOH	7	>95

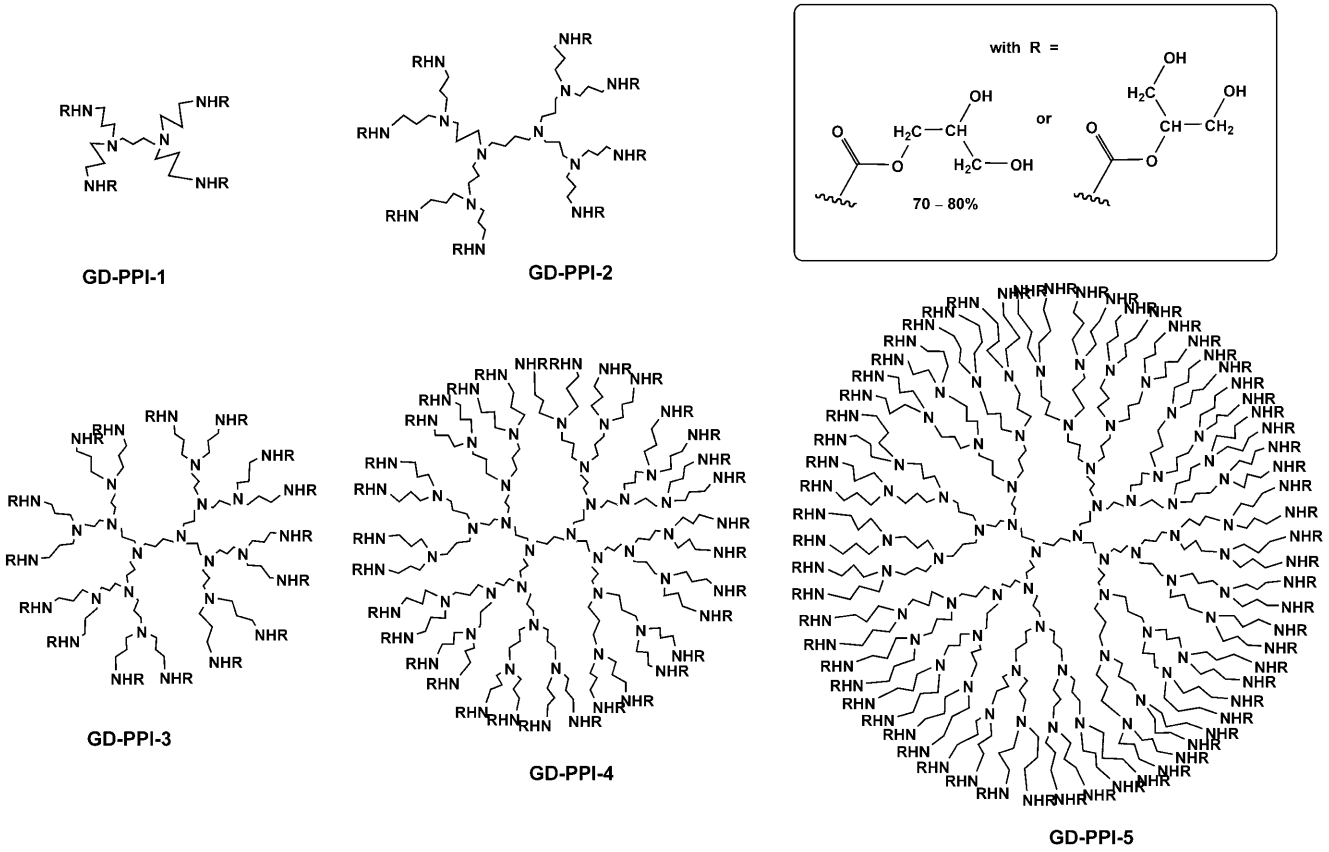
[a] Amount of glycerol carbonate per amino group.

Table 3. Reaction conditions for the synthesis of GD-PPI-2–GD-PPI-5 in MeOH.



Entry	PPI	Equiv. Glycerol carbonate[a]	Equiv. Et_3N	Temp. [°C]	Time [h]	Product	Conv. [%]	Yield [%][b]
1	PPI-2	1.1	–	r.t.	24	GD-PPI-2	76	–
2	PPI-2	1.1	0.7	r.t.	24	GD-PPI-2	96	87
3	PPI-3	1.1	0.7	r.t.	44	GD-PPI-3	76	–
4	PPI-3	1.2	0.7	r.t.	68	GD-PPI-3	85	–
5	PPI-3	2.5	2.5	65	24	GD-PPI-3	98	80
6	PPI-4	2.5	2.5	65	24	GD-PPI-4	99	73
7	PPI-5	2.5	2.5	65	24	GD-PPI-5	98	95

[a] Equivalent of glycerol carbonate was calculated on the basis of -NH_2 group of PPI.
[b] Isolated yields.



Scheme 1. Structures of GD-PPI-1–GD-PPI-5 synthesized in this work.

the synthesis of the second generation GD-PPI-2 led only to 76% conversion of glycerol carbonate at room temperature (Table 3, entry 1). This lower conversion is probably due to the higher steric hindrance of PPI-2. We found that addition of triethylamine to the reaction medium allowed a significant increase in the glycerol carbonate conversion from 76 to 96% (Table 3, entry 2 *vs.* entry 1). Here again, the reaction of PPI-2 with glycerol carbonate was monitored by ^{1}H NMR where a shift of 0.4 ppm of the protons H-8 (2.7 ppm for PPI-2 and 3.12 ppm for GD-PPI-2, see Experimental Section) was observed. After purification by precipitation, the second generation GD-PPI-2 was isolated with 87% yield (Table 3, entry 2).

Synthesis of the higher generation of GD-PPI was more complex and the reaction conditions had to be adapted. Using the above-described procedure for the synthesis of GD-PPI-3, the conversion of glycerol carbonate reached only 76% (Table 3, entry 3). Increasing the amount of glycerol carbonate from 1.1 to 1.2 equiv. resulted in an increase of the glycerol carbonate conversion from 76% to 85% (Table 3, entry 4). Finally, by using a larger amount of glycerol carbonate (2.5 equiv.) while refluxing the mixture for 24 h in methanol, the conversion of glycerol carbonate was nearly complete (Table 3, entry 5). After purification by precipitation, the corresponding GD-PPI-3 was isolated with 80% yield. These optimal conditions were also applied with success to the preparation of GD-PPI-4 and GD-PPI-5 which were isolated with 73 and 95% yields, respectively (Table 3, entries 6 and 7). In the Scheme 1 is represented the structure of the GD-PPI-1–GD-PPI-5 prepared in this work.

The above-described GD-PPI-1–GD-PPI-5 were then tested as homogeneous catalyst in the ring opening of 1,2-epoxydodecane with dodecanoic acid in glycerol. As summarized in Table 4, all GD-PPI-1–GD-PPI-5 were found to be 2.5 times less active than the reference homogeneous catalyst PPI-5 while the selectivity of the reaction remained similar. This decrease of activity might be ascribed to (i) the greater hydrophylicity of GD-PPIs as compared to that of PPI-5 making more difficult their interaction with reactants and (ii) the more difficult accessibility of the nitrogen atoms. It should be noted that no difference of activity was observed between all tested GD-PPIs.

Interestingly, on the basis of the kinetic profiles, we found that an induction period was necessary (Figure 1). Indeed, after nearly 30 min of reaction at 110 °C, the reaction rate was significantly increased. This effect is even more pronounced when the reac-

Table 4. Ring opening of 1,2-epoxydodecane with dodecanoic acid catalyzed by PPI-GD1–GD-PPI-5 in glycerol.

Entry	Catalyst	Time [h]	Conv. [%]	Yield [%][a]
1	–	4.0	30	12
2	PPI-5	4.0	92	69
3	GD-PPI-1	7.5	95	71
4	GD-PPI-2	7.5	95	71
5	GD-PPI-3	7.5	95	72
6	GD-PPI-4	7.5	94	70
7	GD-PPI-5	7.5	95	73

[a] Isolated yields.

tion temperature was decreased to 90 °C. At this temperature, the induction period was about 4 h. We assume that this period of induction corresponds to the formation of an acid-base ion pair between the amino groups of the GD-PPI and the dodecanoic acid. Then the corresponding carboxylate of ammonium plays the role of a phase-transfer agent and accelerates the dissolution of the reactants in the catalytic glycerol phase. Such a phenomenon can be also observed visually. Indeed, after 30 min of reaction, the reaction medium becomes turbide in accordance with the formation of an emulsion (Figure 1).

Next, we examined the influence of the decoration of PPIs with glycerol moieties on their immobilization in glycerol. To this end, recycling experiments were performed. In all experiments, products of the reaction were recovered by liquid-liquid phase extraction with ethyl acetate and reactants were directly reloaded to the glycerol phase. All reactions were stopped after 4 h of reaction.

From Figure 2, it clearly appears that the GD-PPIs are much more retained in the glycerol phase than PPI-5, thus validating our strategy. Interestingly, the recyclability of the GD-PPIs is closely dependent on their generation. Indeed, increasing the generation of GD-PPIs resulted in a better immobilization in the glycerol phase. In particular, the high generation GD-PPI-5 was strongly retained in the glycerol phase, thus allowing a convenient recycling of the catalyst. As illustrated in Figure 2, the GD-PPI-5 catalyst was successfully recycled at least 5 times without an obvious loss of activity. Note that elemental analysis of the recovered ester revealed the absence of nitrogen further confirming that GD-PPI-5 was left in the glycerol phase after the liquid-liquid phase extraction.

Having this GD-PPI-5 in hand, we then tested different acids and epoxides in order to check the versa-

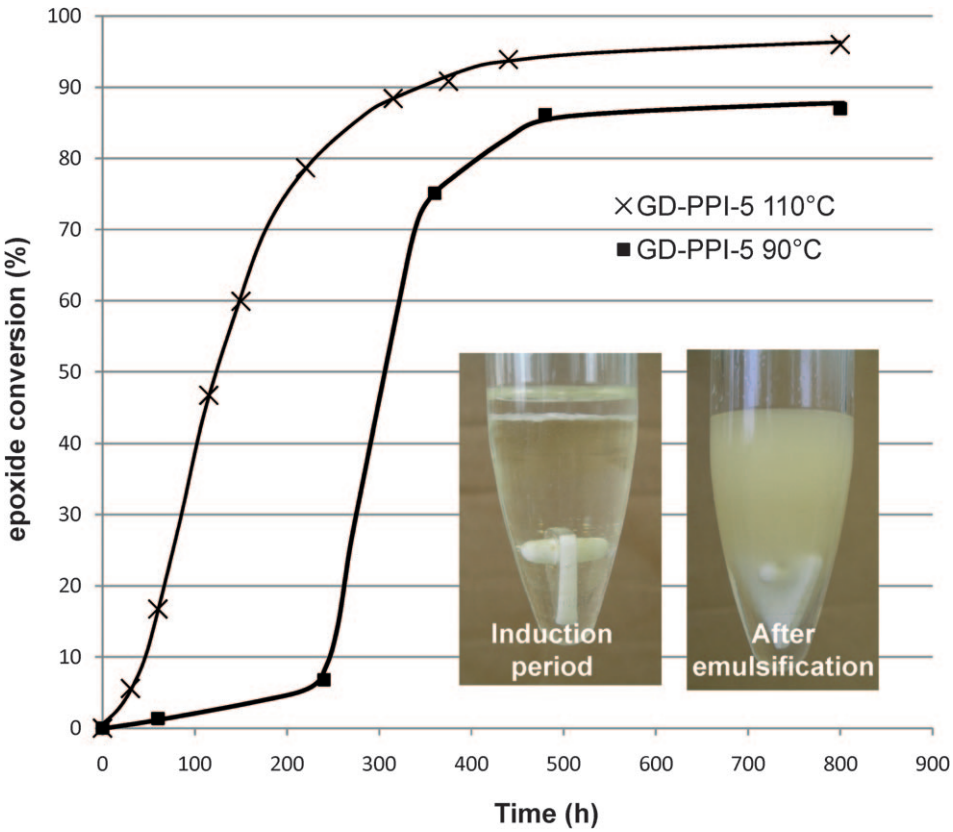


Figure 1. Catalytic activity of GD-PPI-5 at 110 °C and 90 °C. Pictures were taken at 110 °C after stopping of the reaction stirring.

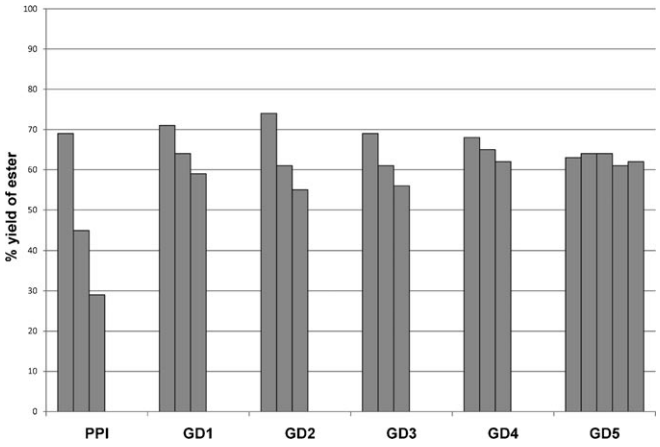


Figure 2. Recycling experiments.

tility of our catalytic system. Results are summarized in the Table 5.

Whatever the considered epoxide or carboxylic acid, the homogeneous catalyst GD-PPI-5 afforded, in glycerol, the corresponding esters with a yield range of 45–70%. To our great delight, in all cases, the esters were selectively extracted from the catalytic phase by liquid-liquid phase extraction with ethyl acetate, thus allowing us to recycle the homogeneous catalyst GD-PPI-5 at least 3 times without an appreciable change of activity.

In conclusion, we have reported here the synthesis of new dendrimers that can be successfully immobilized in glycerol. We found that the high generation of glycerol-decorated PPIs can be successfully immobilized in sustainable and cheap glycerol, thus offering new tools for (i) selectively extracting the reaction products from the glycerol/catalyst phase and (ii) recycling these valuable but expensive dendrimeric-based homogeneous catalysts.

Experimental Section

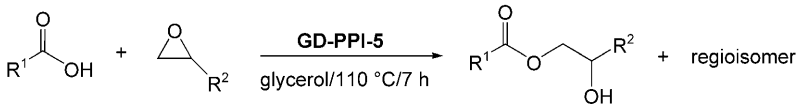
Solvents were distilled and dried under argon. The THF was dried over sodium/benzophenone and the MeOH over sodium. All other commercial products are used as received without further purification. TLC were performed on silica 60 F_{254} Fluka and chromatographies on SDS silica 60 Å (0.060–0.200 mm). ^{1}H and ^{13}C NMR spectra were recorded on an AC 250 Bruker in $CDCl_3$ or DMSO-d_6 as solvents with TMS as reference for ^{1}H spectra and $CDCl_3$ ($\delta = 77.0$) or DMSO-d_6 ($\delta = 39.8$) for $^{13}C\{^1H\}$ spectra. IR spectra were recorded on an AVATAR 320 FT-IR apparatus (KBr pellets or films). Elemental analysis (C, H, N) were realized on a Flash EA-1112 Series.

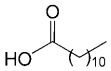
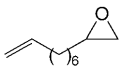
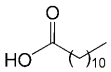
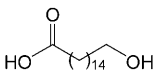
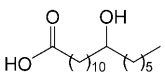
All experiments (MS and HR-MS) were performed on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, UK) operated in the positive mode. The electrospray potential was set to 3 kV in the positive ion mode (flow of injection 5 μL min^{-1}.) and the extraction cone voltage was usually varied between (30–90 V).

General Procedure for Catalytic Experiments

Typically, epoxide (1 mmol) and carboxylic acid (1 mmol) were mixed in 4 mL of glycerol in the presence of the desired GD-PPI (amount of catalytic basic sites introduced: 0.2 equiv. of nitrogen atoms). The resulting mixture was then stirred at 110 °C up to total consumption of the epoxide. At the end of the reaction, the reaction products were directly extracted with ethyl acetate. After evaporation under reduced pressure, the recovered residue was purified over flash silica gel chromatography using a mixture of hep-

Table 5. Generalization of the catalytic process.



Entry	Epoxide	Carboxylic acid	Catalytic run	Yield [%][a]
1			1	71
			2	64
			3	69
2			1	66
			2	65
			3	62
3			1	44
			2	43
			3	45
4			1	50
			2	47
			3	46

[a] Isolated yields.

tane/ethyl acetate (80/20) as eluent. Analytical data of products are provided in the Supporting Information.

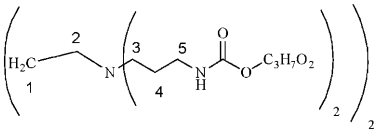
General Procedure for the Catalyst Recycling

At the end of the reaction, the reaction products were extracted from the glycerol/catalytic phase with ethyl acetate (1×4 mL). Then, 1 mmol of epoxide and 1 mmol of carboxylic acid were reloaded. In all recycling experiments, the reaction was stopped after the same reaction time.

General Procedure for the Synthesis of GD-PPI

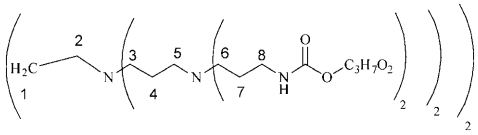
To a solution of PPI dendrimer (1.0 equiv.) in MeOH (2 mL) were added glycerol carbonate (1.25 equiv. per branch) and triethylamine (1.25 equiv. per branch). After stirring the mixture under reflux overnight, the solvent was removed under reduced pressure. The crude product was dissolved in a minimum volume of MeOH, then precipitated with excess of pentane/AcOEt (2:1, v/v). Glycerodendrimers were obtained as pale yellow oils in 78, 87, 80, 73 and 95% yields for GD-PPI-1, GD-PPI-2, GD-PPI-3, GD-PPI-4 and GD-PPI-5 respectively.

Data for GD-PPI-1



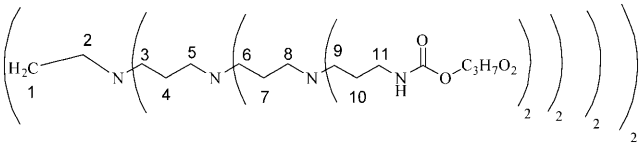
$C_{32}H_{64}N_6O_{16}$: MW 788.88 g mol^{-1}; yield: 78%; ^{1}H NMR (250 MHz, DMSO-d_6, 298 K): $\delta = 1.29$ (4H, s, H-1), 1.47 (8H, s, H-4), 2.29 (12H, s, H-2+H-3), 2.93 (8H, m, H-5), 3.40 (10H, m, H glycerol moiety), 3.88 (8H, m, H glycerol moiety), 4.55 (10H, m, H glycerol moiety), 7.03 (4H, m, NHCO); ^{13}C NMR (62.5 MHz, DMSO-d_6, 298 K): $\delta = 25.9$, 27.5, 51.4, 53.8, 60.5, 63.2, 63.5, 65.9, 70.2, 75.7, 156.5, 156.8; HR-MS: $m/z = 789.4459$, calcd. for $C_{32}H_{65}N_6O_{16}$ [M+H$^+$]: 789.5547; elemental analysis calcd. (%) for $C_{32}H_{64}N_6O_{16}$: C 48.72, H 8.18, N 10.65; found: C 48.47, H 8.24, N 10.36.

Data for GD-PPI-2



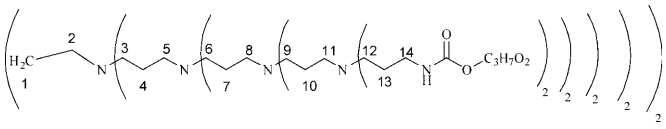
$C_{72}H_{144}N_{14}O_{32}$: MW 1718 g mol^{-1}; yield: 87%; ^{1}H NMR (250 MHz, DMSO-d_6, 298 K): $\delta = 1.29$ (4H, s, H-1), 1.47 (24H, m, H-4+H-7), 2.30 (36H, s, H-2+H-3+H-5+H-6), 2.96 (16H, m, H-8), 3.40 (20H, m, H glycerol moiety), 3.89 (12H, m, H glycerol moiety), 4.50 (24H, m, H glycerol moiety), 7.01 (8H, m, NHCO); ^{13}C NMR (62.5 MHz, DMSO-d_6, 298 K): $\delta = 24.4$, 24.9, 27.4, 51.7, 52.1, 53.8, 60.5, 61.0, 63.2, 63.5, 65.9, 66.3, 70.2, 72.9, 75.6, 77.4, 156.5, 156.8; MS: $m/z = 1713.6$, calcd. for $C_{72}H_{145}N_{14}O_{32}$ [M+H$^+$]: 1718.0; elemental analysis calcd. (%) for $C_{72}H_{144}N_{14}O_{32}$: C 50.34, H 8.45, N 11.41; found: C 49.69, H 8.40, N 10.79.

Data for GD-PPI-3



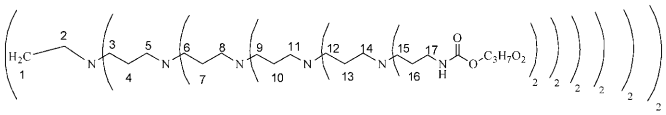
$C_{152}H_{304}N_{30}O_{64}$: MW 3576 g mol^{-1}; yield: 80%; ^{1}H NMR (250 MHz, DMSO-d_6, 298 K): $\delta = 1.40$ (4H, s, H-1), 1.64 (56H, m, H-4+H-7+H-10), 2.49 (84H, s, H-2+H-3+H-5+H-6+H-8+H-9), 3.14 (32H, m, H-11), 3.62 (20H, m, H glycerol moiety), 4.01 (36H, m, H glycerol moiety), 4.84 (32H, m, H glycerol moiety), 7.21 (16H, m, NHCO); ^{13}C NMR (62.5 MHz, DMSO-d_6, 298 K): $\delta = 24.9$, 25.0, 28.0, 51.7, 52.2, 53.0, 61.1, 63.8, 64.0, 66.4, 70.7, 73.4, 76.2, 157.1, 157.3; MS: $m/z = 3568.2$, calcd. for $C_{152}H_{305}N_{30}O_{64}$ [M+H$^+$]: 3575.1; elemental analysis calcd. (%) for $C_{152}H_{108}N_{30}O_{64}$: C 51.05, H 8.57, N 11.75; found: C 50.25, H 8.82, N 11.54.

Data for GD-PPI-4



$C_{312}H_{624}N_{62}O_{128}$: MW 7293 g mol^{-1}; yield: 73%; ^{1}H NMR (250 MHz, DMSO-d_6, 298 K): $\delta = 1.40$ (124H, s, H-1+H-4+H-7+H-10+H-13), 2.25 (180H, s, H-2+H-3+H-5+H-6+H-8+H-9+H-11+H-12), 2.87 (64H, m, H-14), 3.60 (148H, m, H glycerol moiety), 4.60 (76H, m, H glycerol moiety), 6.94 (32H, m, NHCO); ^{13}C NMR (62.5 MHz, DMSO-d_6, 298 K): $\delta = 24.4$, 24.5, 27.4, 51.4, 51.7, 52.1, 52.2, 60.5, 63.2, 63.5, 65.9, 70.2, 72.9, 75.7, 156.3, 156.8; elemental analysis calcd. (%) for $C_{312}H_{624}N_{62}O_{128}$: C 51.39, H 8.62, N 11.97; found: C 50.34, H 8.68, N 11.79.

Data for GD-PPI-5



$C_{632}H_{1200}N_{126}O_{256}$: MW 14661 g mol^{-1}; yield: 95%; ^{1}H NMR (250 MHz, DMSO-d_6, 298 K): $\delta = 1.34$ (252H, s, H-1+H-4+H-7+H-10+H-13+H-16), 2.18 (372H, s, H-2+H-3+H-5+H-6+H-8+H-9+H-11+H-12+H-14+H-15), 2.87 (128H, m, H17), 3.60 (224H, m, H glycerol moiety), 4.60 (224H, m, H glycerol moiety), 6.94 (64H, m, NHCO); ^{13}C NMR (62.5 MHz, DMSO-d_6, 298 K): $\delta = 25.7$, 25.8, 28.8, 28.9, 53.0, 53.2, 53.5, 53.5, 53.6, 53.8, 53.9, 62.1, 64.8, 65.1, 67.5, 71.8, 74.5, 77.2, 158.1, 158.4; elemental analysis calcd. (%) for $C_{632}H_{1264}N_{126}O_{256}$: C 51.53, H 8.66, N 11.99; found: C 51.72, H 8.73, N 12.53.

Acknowledgements

This work was supported by the CPER framework (Pentoraf program). We are grateful to the Public Authorities of Champagne-Ardenne and FEDER for material funds and fellowship to S.B. The authors also acknowledge the CNRS and French Ministry of Research for their financial support. RDS is also grateful to the Agence National de la Recherche (action no. ANR-07-CP2D-07-02) for his PhD grant.

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