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Precise 2D-patterned Incompatible Catalysts for Reactions in One-pot

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We show precise and direct two-dimensional (2D) printing of the incompatible polymer acidbase catalysts and their utility in one-pot two-step reactions. Multi-step catalytic reactions using incompatible catalysts in a one-pot reaction cascade require special methods and materials for isolation of catalysts from each other. This, in general is a tedious process requiring special polymer architectures as catalysts' carrier for preserving the activity of otherwise incompatible catalysts. We propose the immobilization of incompatible polymer catalysts, such as polymer acid and base catalysts, on a substrate in variable sizes and amounts by precise 2D printing. The copolymers with a basic (4-vinylpyridine) and acidic (styrene sulfonic acid) functionality and methacryloyl benzophenone as a UV cross-linking unit were used for 2D printing on poly (ethylene terephthalate) (PET). The printed meshes were immersed together in a reaction solution containing (dimethoxy methyl)-benzene and ethyl cyanoformate, resulting in a twostep acid-base catalyzed cascade reaction, i.e. deacetalization followed by carbon-building reaction. The time-dependent consumption of (dimethoxymethyl)-benzene to the intermediate benzaldehyde and the product was monitored, and a kinetic model was developed to investigate the underlying reaction dynamics. The complexity of multi-step Wolf-Lamb-type reactions was generally significantly decreased using our approach due to the easy polymerization and immobilization procedure.

1. Introduction

Mutually incompatible functional groups, such as acid and base, deactivate each other in solution. When used as catalysts for organic reactions in one-pot, they lose their catalytic activity. Such catalysts are called Wolf-Lamb-type catalysts. The work of Patchornik opened up new possibilities of making one-pot reactions with incompatible catalysts of Wolf-Lamb-type by immobilizing them on solid supports.^[1,2] The catalysts become mutually active and do not interfere with each other's catalytic activity if immobilized separately on two different solid supports which do not come into contact or on one support in a site-isolated manner. This is highly desirable for cascade reactions in one-pot in which the catalysts (more than one) and reactants, combined in one reactor, undergo a sequence of precise catalytic steps.

The site-isolated spatial positioning of the catalysts to prevent their deactivation in a simple way requires new concepts. Polymeric microcapsules are interesting carriers for the site-isolation of two incompatible catalysts.^[3] Microporous organic nanotube networks made by hyper cross-linking core–shell bottlebrush copolymers immobilized with site-isolated acid and base catalyst systems showed good catalytic performance for deacetalization-Knoevenagel cascade reactions.^[4] The core and cross-linked shell of self-assembled amphiphilic triblock copolymers can also be used as separate compartments for the site-isolation of metal catalysts. Instead, the catalysts can be immobilized in the core of star polymers and a mixture of star polymers with different core catalysts (acids and bases) can also be used as site-isolated catalysts in one-pot reactions.^[5,6] Mesoporous silica support with acid and basic groups and sol-gel have also been used for one-pot cascade reactions.^[7-9] Compartmentalization by layered

Pickering emulsion was recently achieved for carrying out cascade reactions in one-pot. The acid and base catalysts were immobilized in droplets in different layers avoiding contact with

each other.^[10,11] Layer-by-layer self-assembly is another interesting approach to build multicomponent thin films for cascade reactions.^[12]

Although some research progress has been achieved over the years, one-pot multistep reactions are still not generally applicable in chemo- or bio-catalysis due to the time-consuming special procedures required for making appropriate carriers. New, efficient and scalable carrier systems for cascade reactions which are experimentally feasible in a simple way are always sought.

We recently used electrospun acid and base nonwovens, for a two-step Wolf-Lamb type catalytic reaction sequence in one-pot. The individual acid and base nonwovens fixed on separate frames were inserted in the reaction medium in one-pot.^[13]

Three-dimensional (3D) printing offers the possibility of precise material structuring, and size and shape modulations which can be of high utility in heterogenous catalysis. Coelho et al. have combined the 3D printing of silica monolith and post-printing surface modifications with palladium and copper metals for catalysis.^[14] The use of 3D printing in making structured catalysts and reaction reactors has been reviewed recently.^[15] The inactive scaffolds are generally produced by 3D printing, followed by the incorporation of functional groups for catalysis in a post-printing step.^[16,17]

Slowing et al. printed directly functional monomers followed by ultraviolet (UV) cross-linking for making reactor parts for catalytic applications.^[18] We show here the 2D patterning of Wolf-Lamb-type catalysts on a neutral substrate by direct printing of Wolf-Lamb-type (acid and base) catalytically active polymers and their use in a two-step one-pot reaction. The reaction sequence tested was the standard deacetalization of (diemethoxymethyl)-benzene as the first step and C-C bond formation as the second step. The separation between the 2D printed acid-

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base catalysts is achieved by fixing individual printed membranes in a reaction flask in onepot. The technique can be easily extended in a modular way with more than two catalysts for multi-step reactions in the future.

2. Discussion and results

The acidic and basic copolymer catalysts were synthesized by free radical ter-copolymerization of styrene, 4-vinylpyridine (basic, Scheme 1 I) or styrene sulfonic acid (SSA) (acidic, Scheme 1 II/III) units and methacryloyl benzophenone (MABP) to enable post-processing cross-linking of the polymer to prevent it from dissolving and to let the 2D-printed structures swell in reaction solution, which is necessary to enable high reachability to the catalytic sites in the bulk. MABP is a photoreactive cross-linker, very well-known in the literature for the cross-linking reactions.^[19] The benzophenone unit of MABP forms radicals by photoillumination, followed by abstraction of C-H hydrogen from the polymer chain and then radical combination reactions leading to cross-linking as shown in Scheme S1 in SI. The molecular weight (M_n) was 52000 with a molar mass dispersity (Đ) 1.7 (Supporting information, Figure S1). The copolymer compositions as determined by ¹H-NMR for basic terpolymer is 47 % 4vinylpyridine, 42 % styrene and 11 % 4-benzoylphenyl methacrylate (Supporting information, Figure S2). The copolymer composition for acid terpolymer could not be determined through only ¹H-NMR (Supporting information, Figure S3) due to the overlapping peaks. Therefore, elemental analysis was used to determine the amount of SSA to be around 16 mol%; with ¹H-NMR, and the amount of styrene and MABP was calculated to be 71 mol% and 13 mol%, respectively. The molecular weight determined (M_n) was 124000 with a molar mass dispersity (Đ) 1.7 (Supporting information, Figure S4).



Scheme 1. Free radical copolymerization for the formation of polymeric base (I) and acid (II). The copolymers individually were dissolved in a mixture of THF and DMF (9 to 1 with 20 wt% in the case of acid copolymer, viscosity at 26 Pa s at a shear rate of 10 s⁻¹ and 30 wt% in the case of base copolymer, viscosity at 0.3 Pa s at a shear rate of 10 s⁻¹ (Supporting information, **Figure S5**)).

The polymers are separately patterned on commercial poly(ethylene terephthalate) (PET) mesh with a line width of 120 μ m (**Figure 1**) followed by UV cross-linking. The patterned structure

shows a good alignment with the printing file (Supporting information, **Figure S6**). The 3D printer Celllink Inkredible+ was used for patterning the catalysts.



Figure 1. Digital photographic image of the patterned printed structure used. (A) is for the acid copolymer and (B) is for the basic copolymer.

The patterned cross-linked samples had about 3 mg of the catalytic polymers per cm², which leads to 12 μ mol in the case of the basic catalyst (4-VP units) and 6 μ mol in the case of the acidic catalyst (SSA units) per cm². The samples were analyzed using microscopy and Raman imaging (**Figure 2 and 3**; microscopic stitching images are shown in the supporting information, **Figure S7**). The position of the acid and basic polymer catalysts could be identified utilizing Raman measurements. The acid polymer catalyst p(S-*co*-SSA-*co*-MABP) was deposited between the cavities of the PET mesh (Figure 2 B, C) separated by PET spacers with only a very thin layer on top of the PET structure.



Figure 2. Microscopy image of the 3D-printed acid copolymer with a white line showing the place used for Raman imaging (A), the Raman spectrum for PET (red) and acid copolymer (blue) (B) and the Raman imaging for the 2D-printed structure indicating high amounts of the copolymer in between the meshes (C).

The microscopy images and the Raman spectra (Figure 3A and 3B) showed the deposition of the polymer in the cavity between the PET spacers and on top of the PET for the basic polymeric catalyst. The polymer catalysts deposited between the PET spacers have a high accessibility from both sides.



Figure 3. Microscopy image of the 3D-printed basic polymer (A) with a white line indicating the measured position in Raman imaging, the Raman spectrum for PET (blue), basic polymer (green) and for the white box within image the Raman imaging (red), in which the red part is the PET mesh and the blue part the 3D-printed polymer (C).

The patterned cross-linked polymer catalysts were immersed in DMF to check their solvent stability and the structures were monitored afterwards utilizing microscopy images (**Figure S8**). The structures were stable after immersion in DMF and a swollen state was observed. The swelling of the polymers should be advantageous for the catalytic experiment because the swollen 2D-printed structure would have good accessibility to catalytic sites.

Subsequently, the patterned acid-base (Wolf-Lamb-type) catalysts were tested for their activity by performing deacetalization and the formation of cyano(phenyl)methyl ethyl carbonate (twostep) reactions in one-pot. The first step was catalyzed by acid and the second by base (Scheme 2). The reactions were followed by gas chromatography (GC) measurements with the help of undecane as an internal standard.



Scheme 2. Two-step reaction sequence catalyzed by incompatible acid and base catalysts : first step- deacetalization of (dimethoxy)methyl benzene to benzaldehyde (acid catalyzed), second step- C-C bond formation by reaction of ethyl cyanoformate and benzaldehyde (base catalyzed).

Firstly, the individual acid catalysts were used in different amounts (**Figure 4**). The acid catalyzed deacetalization was fast: 50 % conversion to benzaldehyde was achieved in 10 min using 15 mg of the acid catalyst (16 μ mol, 0.75 mol% SSA, Figure 4A green x). The rate increased further on increasing the amount to 30 mg (32 μ mol, 1.5 mol% SSA, Figure 4A blue cross) and 90 % benzaldehyde was produced in 10 min. Subsequently, the two-step system was established. The pure acidic reactions were compared with the acidic part of a Wolf-Lamb-type two-step reaction leading to the result that the reaction was slower using the same amount of acidic catalyst (30 mg; Figure 4A green "x" for pure acidic reaction) but faster than using half of the amount (15 mg; Figure 4A blue "+" symbol), indicating a slight deactivation due to water within the reaction chamber, which is unavoidable as it is necessary for the deacetalization reaction. Still, the reaction produced more than 90 % benzaldehyde in 60 min.



Figure 4. Consumption of the deacetalization from (dimethoxy)methyl benzene to benzaldehyde in a single step reaction. The reaction stops after 60 min with a consumption of over 95 % (A), the catalytic load was 1.5 mol% (green x) and, respectively, 0.75 mol% (blue +). A comparison shows that similar results are obtained for 2D-printed structures in two-step reactions. (B) Partial deactivation is observable as the resulting time consumption curve (1.5 mol L⁻¹ catalytic load) is faster than the blue crosses, but slower than the green x. The reaction condition for all experiments was 80 °C and consumption was monitored using GC; all reagents were dissolved at the beginning.

As a model reaction, the deacetalization described already was further followed by a basic catalyzed reaction of benzaldehyde and ethyl cyanoformate (Scheme 2), which led to the formation of a carbonate group. Here, the study was performed with 30 mg (1.5 mol% of SSA groups) of acidic catalyst and 60 mg (9.6 mol% of 4-vinylpyridine groups) of basic catalyst.



Figure 5. Two-step Wolf-Lamb-type reaction showing the amount of benzaldehyde (blue circle) and cyano(phenyl)methyl ethyl carbonate (green triangles). The amount of catalyst used was 1.3 mol% (30 mg acid terpolymer) styrene sulfonic acid and 9.6 mol% 4-vinylpyridine (60 mg base terpolymer). The catalytic reaction was performed at 80 °C, all reagents and catalysts were immersed at the beginning and the amount was monitored utilizing GC.

As expected, the amount of benzaldehyde increases towards a maximum at around 60 min with an amount of around 80 % (**Figure 5**). The amount of cyano(phenyl)methyl ethyl carbonate increases significantly after 60 min until the maximum is reached at 250 min with a conversion of 62 %. The low conversion can be explained by the low basicity of 4-vinylpyridine, which can be improved in future by using a strong base. Furthermore, it was possible to show that it is possible to restart the basic reaction by the addition of ethyl cyanoformate (Supporting information, **Figure S10**), possibly due to an effect of equilibrium in combination with a low catalytic load.

Kinetical studies were carried out to gain a greater understanding. The reactions were fitted with differential equations describing the reaction rates (equation 1-5).

$$\frac{dc_A}{dt} = -k_1 c_A(t) c_B(t) \tag{1}$$

$$\frac{dc_B}{dt} = -k_1 c_A(t) c_B(t) \tag{2}$$

$$\frac{dc_C}{dt} = k_1 c_A(t) c_B(t) - k_2 c_C(t - \Delta t) c_D(t)$$
(3)

$$\frac{dc_D}{dt} = -k_2 c_C (t - \Delta t) c_D(t) \tag{4}$$

$$\frac{dc_E}{dt} = k_2 c_C (t - \Delta t) c_D(t) \tag{5}$$

Here, c_A is the concentration of (dimethoxy)methyl benzene, c_B is the concentration of water, c_C is the concentration of benzaldehyde and c_D is the concentration of ethyl cyanoformate. k_I and k_2 are the reaction rates of the first and second reaction step, respectively. The necessity of a parameter Δt was already described in our previous work for this specific reaction.^[13] There, we were able to show that the retarded start needed to be expressed by this specific parameter, as otherwise, no reasonable fits were obtained. A retarded start is generally expected for such reactions.^[20,21]

The resulting fitted parameters (**Table 1**) are close to the experimental values. Only the value for water (c_{B0}) is much lower (0.44 mol L⁻¹) compared to the experimental value of 1 mol L⁻¹. A possible explanation is the adsorption of water within the printed structures leading to a decrease of its availability. The fits show a reasonable alignment with the data (**Figure 6**).

Parameter	Fitted value
C _{A0}	0.48 mol L ⁻¹
C_{B0}	0.44 mol L ⁻¹
C_{D0} (fixed)	0.6 mol L ⁻¹
Δt	39 min
k_1	0.51 mol (L min) ⁻¹
<i>k</i> ₂	0.01 mol (L min) ⁻¹

Table 1. Resulting fitted parameters after solving equation 1-5.



Figure 6. Kinetical fitted parameters of the two-step cascade reaction catalyzed by incompatible acid-base catalysts: red, blue and green are the amounts of (dimethoxy)methyl benzene, benzaldehyde and cyano(phenyl)methyl ethyl carbonate, respectively.

3. Conclusion

The 2D-printed structures were shown to be suitable carrier material for incompatible acidbase catalysts for one-pot cascade reaction sequence. The polymers reacting as acid and base catalysts were made by free radical polymerization and 2D printing on top of a PET mesh was done using a 3D printer. Here, we were able to characterize the 2D-printed structures by optical microscopy and Raman studies. The polymer-carrying meshes were immersed in the reaction solution for the two-step reaction. Although, both reaction steps were achieved in parallel, but the second step showed a retarded start of 50 min. The overall conversion was around 90 % for the first step and 62 % for the second step. Subsequently, a kinetic model was designed to observe the underlying reaction dynamics. The complexity of such systems was significantly decreased with our approach due to the easy polymerization and immobilization techniques used.

The conversions need to be improved in future studies to obtain a higher overall yield. Functionality of the basic monomer can be changed towards, for example, amine-based

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comonomers, as done by other groups, to increase the amount of reactions that can be catalyzed. Overall, a great toolkit for such catalytic reactions was achieved which is usable for further studies.

4. Experimental Section

Materials

The DMSO (p.a. grade), THF (p.a. grade) and DMF (p.a. grade) were purchased from Alfa Aesar and used as received. The 4-vinylpyridine (98 %) and styrene were purchased from Sigma Aldrich and distilled *in vacuo*. Sodium styrene sulfonate (90 %, Alfa Aesar) was recrystallized from a mixture of ethanol and water (90/10 volume%). The ethyl cyanoformate (98 % Alfa Aesar), dimethoxybenzylacetal (99 %, Alfa Aesar) and undecane (> 99 %, Alfa Aesar) for the catalytic experiments were used as received.

Methods

Nuclear magnetic resonance (NMR) spectroscopy: ¹H-NMR experiments were recorded on a Ultrashield-300 spectrometer at room temperature in either CDCl₃ or DMSO-d₆. Spectra were calibrated according to the residue protons of the deuterated solvent signal. Evaluation of spectra was carried out with MestReNova (Mestrelab research, version 6.1).

The 3D printing was performed with a Celllink Inkredible+ with a one-needle setup. Solutions were 20 wt% for poly(S-*co*-SSA-*co*-MABP) and 30 wt% for poly(S-*co*-4VP-*co*-MABP) in THF/DMF (90/10). A pressure of 170 kPa was used for polymer solution flow through the syringe. The solutions were printed on a PET mesh with a mesh width of 120 μ m. The printed structure was cross-linked for 3 h under UV light with an UV-F 400 F (honle UV technology) from the top side of the samples.

Optical Microscope images were taken by a Smartzoom5 (Zeiss).

Size Exclusion Chromatography (SEC) measurements were performed in DMF (HPLC grade) with lithium bromide (5 g L⁻¹) as an eluent and solvent and an internal standard of toluene on 2 PSS-GRAM gel columns (particle size = 10 μ m) with a porosity of 100 to 3000 Å, a flow rate of 0.5 mL min-1 and a refractive index detector (Agilent Technologies) on a SEC 1260 Infinity (Agilent Technologies). A narrowly distributed polystyrene homopolymer was used (PSS calibration kit) for calibration.

Gas Chromatography (GC): The GC measurements were performed on a GC-FID system (GC-2010 Plus, Shimadzu), using nitrogen as a carrier gas. An amount of 10 μ L of the reaction mixture was dissolved in 1 mL acetonitrile. A volume of 1 μ L was injected with a split ratio of 1:50 and measured from 50 °C (2-min hold) up to 300 °C with a heating rate of 15 K min⁻¹.

Raman imaging was performed with a WITec alpha 300 RA+ imaging system with a UHTS 300 spectrometer and a back-illuminated Andor Newton 970 EMCDD camera. An excitation wavelength of $\lambda = 352$ nm and an integration time of 0.5 s pixel⁻¹ was used.

Rheology was measured with a Modular Compact Rheometer MCR 302 (Anton Paar) using a standard Measuring System CC17 (concentric cylinder) with a shear rate starting at 0.01 s⁻¹ to 100 s^{-1} with 5 points per decade. Points were measured starting with 20 s down to 5 s during measurements.

MatLab Version 2015a was used for the fitting of the differential equations.

Synthesis of cross-linkable base polymer

The 0.1 eq methacryloyl benzophenon was placed in a round-bottom Schlenk flask and dissolved in THF. The 0.4 eq styrene and 0.5 eq 4-vinylpyridine were added to the mixture subsequently and the reaction mixture was degassed with Argon for 30 min (the concentration of monomers was 4 mol L^{-1}). The reaction mixture was heated to 60 °C, 0.8 wt% AIBN was added and it was stirred for 16 h. The polymer was precipitated in diethyl ether, the resulting

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polymer was redissolved twice in DMSO and precipitated in diethyl ether. The crude product was then dried at 60 °C *in vacuo*.

¹H NMR (300 MHz, CDCl₃, δ): 1.0–1.6 (polymer backbone, CH₂; CH₃); 1.6–2.5 (polymer backbone CH); 6.0–6.6 (aromatic, CH); 6.6–7.2 (aromatic, CH); 7.4–7.7 (aromatic CH;); 8.1–8.5 (aromatic, CH).

Synthesis of cross-linkable acid polymer

The 0.1 eq methacryloyl benzophenone and 0.15 eq recrystallized sodium styrene sulfonate were placed in a round-bottom Schlenk flask and dissolved in DMSO. The quantity of 0.75 eq styrene was added to the solution and the reaction mixture was degassed with argon, heated to 70 °C and 0.6 wt% AIBN was added. The polymer was then precipitated in Isopropanol and dried at 60 °C *in vacuo*.

The crude product obtained was dissolved in methanol and concentrated HCl solution was added dropwise to obtain a white solid. The product obtained was filtered and dried at 60 °C *in vacuo*.

¹H NMR (300 MHz, DMSO-d₆, δ): 0–1.6 (polymer backbone, CH₂; CH₃); 1.6–2.5 (polymer backbone CH); 6.0–6.6 (aromatic, CH); 6.6–7.2 (aromatic, CH); 7.4–7.7 (aromatic, CH).

Catalytic experiment two-step system

The 3D-printed structures (30 mg (1.5 mol%) of the acidic poly(styrene-*stat*-SSA-*stat*-methyl acryloyl benzophenone)) and 60 mg (9.6 mol% of (dimethoxymethyl)benzene) of the basic poly(styrene-*stat*-4-vinylpyridine-*stat*-methyl acryloyl benzophenone) on PET meshes were added into a 10 mL vial.

A solution of 1 eq dimethoxybenzylacetal was dissolved in DMF (c = 0.5 mol/L) and, subsequently, 1.2 eq ethyl cyanoformate, 2 eq water (Milli-Q) and undecane as an internal standard were added for the catalytic experiments. The reaction mixture was heated to 80 °C and the immobilized nonwoven structures were immersed in the reaction medium.

Conflict of interest

The authors have no conflict of interest to declare.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors.

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The 2D patterned structures were used as Wolf-Lamb-type catalysts. Here, an acid and base polymer were synthesized, printed on separate PET, cross-linked by UV light and then immersed in solution to monitor the kinetic of such a multi-step one-pot catalysis. The kinetical constants were calculated using differential equations.

Keyword heterogenous catalysis

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