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PAPER

JandaJel as a polymeric support to improve the catalytic efficiency of immobilized-1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) under solvent-free conditions†

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JandaJel, with its greater spacing between the linear polymeric chains compared to that of polystyrene matrices, is a very efficient support for improving the catalytic efficiency of TBD under SolFC.

Introduction

Among the factors that regulate the activity of a polymer-bound catalyst, the nature of the support is undoubtedly fundamental and in several cases can define the success or the failure of the catalyst itself.[1] Immobilization on a polymeric matrix produces steric and electronic modifications of the catalyst framework, generally but not always, resulting in a consistent reduction of its efficiency.[1]

Swelling of the resin by the reaction medium is considerably influenced by the structure and the conformation of the support facilitating or hampering the access of the reactants to the active sites.[1]

To minimize these possible drawbacks, many polymeric modifications have been proposed, so that a more "solution-like" microenvironment around the catalyst could be created. Interesting results have been obtained, for example, by using linear soluble supports as PEG or NCPS,[1b,1e,2] but in some cases, the catalytic efficiency that results is strictly dependent on the spatial folding of the polymeric chains that may interact with the reaction partners influencing the process course.

Styrene-based resins are the most widely used supports, thanks to their easy availability and high loading capacity. Access impediments can be reduced by increasing the distance between the catalytic site and the polymeric matrix, through the introduction of spacers (generally PEG) of several dimensions, as in the case of Tentagel and Argogel, minimizing thus the swelling problems when polar solvents are used.[1b,1c,1f] However, even in this case, it has been frequently observed that not-inert and conformationally-unstable linkers can negatively influence the process and, sometimes, these resins are difficult to separate from a polar reaction medium because of the PEG hygroscopic nature. Another interesting solution consists of the replacement of 1,4-divinylbenzene (DVB) with alternative cross-linkers characterized by larger dimensions, flexibility and compatibility with several solvent classes.[1b,1c,3,4] In this context, excellent swelling properties have been reached by preparing polystyrene polymers using PEG[1b,1c,3] or polytetrahydrofuran-based (JandaJel resins) cross-linkers.[1b,4]

In the last few years the attention has been principally turned to the JandaJel (JJ) resins, that are chemically more stable and ease to prepare than polyethylene glycol-based ones. These polymers have been successfully used for solid supported organic synthesis (SPOS)[5] and as supports for catalysts in a variety of synthetic transformations,[6] showing a better propensity to be swelled by the solvent and a greater diffusion value than the classical Merrifield resins, with remarkable advantages in terms of reactivity.

We are interested in the development of environmentally and chemically efficient methodologies by exploiting the unique properties of water as reaction medium[7] and solvent-free conditions (SolFC)[8] to realize multigram continuous-flow processes[8a,b,e] characterized by minimal waste production (low E-factor).[9]

Some years ago we have proposed an alternative solution to resin swelling problems that concerns the adoption of SolFC.[8l] Since then, we have contributed in this direction proving that in several cases the efficiency of an anchored catalyst under SolFC is higher than in the presence of a reaction medium, where often the process cannot even be realized satisfactorily.[8a-e,i,l] Besides the high chemical efficiency, the protocols reported feature low E-factors.[8a,b,e] To further reduce waste, our approach was

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† Electronic Supplementary Information (ESI) available: Characterization data for catalysts **1a–g**, characterization data and copies of the ^{1}H and ^{13}C NMR spectra for compounds **10**, **11**, **12**, **18**, **19**, **20**, **29**. See DOI: 10.1039/c1gc15790f/

also exploited in the setting of cyclic continuous-flow protocols operating in SolFC or highly concentrated conditions and running on a multigram scale.[8a,b,e]

We are interested in studying novel polymer supports more suitable for being used under SolFC and in continuous-flow processes than the classic Merrifield resins. The resulting immobilized catalysts should be recoverable, reusable and sufficiently efficient to allow the use of equimolar amounts of reactants and minimize the use of organic solvent for the recovery of the product.

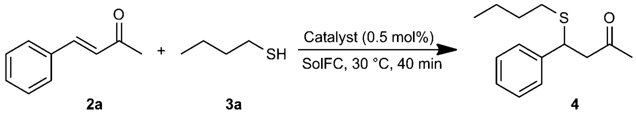
With this goal in mind, we have evaluated the influence of the polymer mesh size and/or the cross-linking nature and percentage on the catalyst activity under SolFC. We have selected the representative base 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) that in its polystyrene-supported version is a well-known catalyst.

Results and discussion

To this purpose, JJ-TBD **1a–d** (1,4-bis(vinylphenoxy)-butane-cross-linked) and PS-TBD **1e–g** (DVB-cross-linked) have been prepared and characterized by elemental analysis, IR spectroscopy and scanning electron microscopy (SEM) (see supporting information†).

Their efficiency has been evaluated and compared also to commercially available Si-TBD (silica gel-supported TBD) **1h** (Scheme 1) in representative C–S bond forming processes as the sulfa-Michael addition (SMA) of (*E*)-benzylideneacetone (**2a**) and 1-butanethiol (**3a**) (Table 1) and the thiolysis of 2,3-epoxypropyl-phenylether (**5a**) by thiophenol (**3b**) (Table 2).

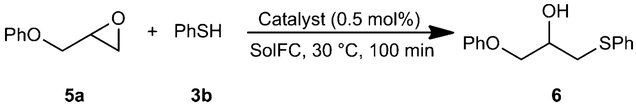
Table 1 Michael addition of 1-butanethiol (**3a**) to (*E*)-benzylideneacetone (**2a**)[a]



Entry	Catalyst	Conversion[b] (%)	Yield[c] (%)
1	**1a**	>99	98
2	**1b**	>99	98
3	**1c**	94	96[d]
4	**1d**	99	98
5	**1e**	<1	—
6	**1f**	2	—
7	**1g**	<1	—
8	**1h**	21	—
9[e]	**1a**	—	—
10[f]	**1a**	—	—

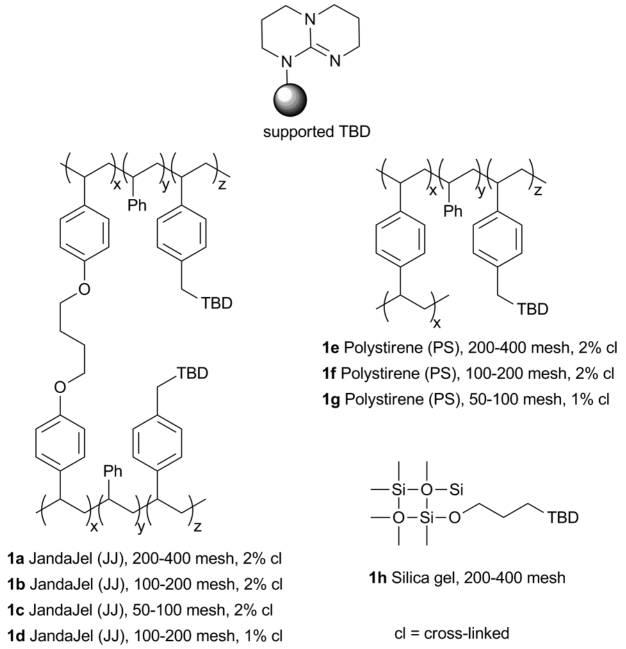
[a] Reaction conditions: **2a** (1.0 mmol), **3a** (1.0 mmol), catalyst (0.5 mol%), 30 °C. [b] Determined by GC analyses. [c] Yield of the isolated pure product. [d] Determined after completion occurred in 80 min. [e] Reaction conducted in CH_2Cl_2 (2.0 mL). [f] Reaction conducted in CH_3CN (2.0 mL).

Table 2 Thiolysis of 2,3-epoxypropyl-phenylether (**5a**) by thiophenol (**3b**)[a]



Entry	Catalyst	Conversion[b] (%)	Yield[c] (%)
1	**1a**	94	96[d]
2	**1b**	>98	97
3	**1c**	>98	97
4	**1d**	>98	97
5	**1e**	28[e]	—
6	**1f**	25[e]	—
7	**1g**	30[e]	—
8	**1h**	88	—
9[f]	**1a**	—	—
10[g]	**1a**	20	—

[a] Reaction conditions: **5a** (1.0 mmol), **3b** (1.0 mmol), catalyst (0.5 mol%), 30 °C. [b] Determined by GC analyses. [c] Yield of the isolated pure product. [d] Determined after completion occurred in 140 min. [e] Complete conversion of **5a** to **6** was reached after 10 h. [f] Reaction conducted in CH_2Cl_2 (2.0 mL). [g] Reaction conducted in CH_3CN (2.0 mL).



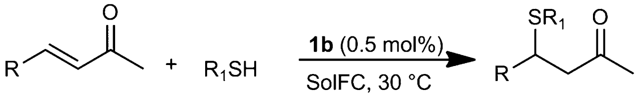
Scheme 1 Polymer-supported-TBD **1a–g** and silica gel-supported-TBD **1h**.

We found that highly promising JJ polymers were in line with our expectations when used under SolFC. JJ-supported TBD **1a–d** was far more efficient than the PS-supported parents **1e–g** (Table 1, entries 1–4 *vs.* 5–7). Under SolFC catalytic performances are strongly determined by the nature of the cross-linker and, in particular, as its size increases, the reactants' access to the active sites is greatly facilitated. Silica gel-supported TBD **1h** gave only a slightly better result than PS-TBD **1e–g** (Table 1, entry 8).

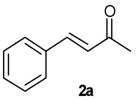
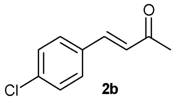
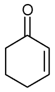
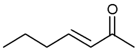
It should be noted that the reactions mediated by PS-TBD **1e–g** and silica-TBD **1h** were extremely slow and, in all cases, the complete conversion was not reached at all after long reaction times.

In the case of JJ-TBD **1a–d**, a substantially identical catalytic efficiency is observed, suggesting that neither the bead sizes variation (Table 1, entries 1–3), nor the slightly different cross-linking percentage used in this study (Table 1, entries 2 *vs.* 4), markedly influenced the catalyst behaviour. Moreover, in all cases, the product was isolated in high yields (96–98%) and purity (≥ 98%) simply by filtration of the reaction mixture.

Table 3 Michael addition of thiol **3a–d** to enones **2a–d** catalyzed by polymer-supported-TBD **1b**[a]



2a-d **3a-d** **4-21**

Entry	Enone	Thiol	Product	t (h)	Yield[b] (%)
1	 **2a**	**3a**: *n*-BuSH	**4**	0.7	98
2		**3b**: C_6H_5SH	**7**	1	97
3		**3c**: 4-Me-C_6H_4SH	**8**	1	93
4		**3d**: $C_6H_5CH_2SH$	**9**	8	91
5[c]	 **2b**	**3a**	**10**	2	96
6		**3b**	**11**	4	99
7		**3c**	**12**	6	96
8[c]		**3d**	**13**	2	95
9	 **2c**	**3a**	**14**	0.3	91
10		**3b**	**15**	0.5	94
11		**3c**	**16**	1	97
12		**3d**	**17**	6	93
13[c]	 **2d**	**3a**	**18**	4	88
14		**3b**	**19**	0.5	98
15		**3c**	**20**	1	97
16		**3d**	**21**	8	90

[a] Reaction conditions: enone (1.0 mmol), thiol (1.0 mmol), catalyst (0.5 mol%), 30 °C. [b] Yield of the isolated pure product. [c] 2 mol% of catalyst were used.

By using 0.5 mol% of catalyst **1b** in the presence of an organic medium (dichloromethane and acetonitrile) a dramatic drop of the catalytic efficiency was observed (Table 1, entries 9–10 respectively).

Catalyst **1b** was also reused in subsequent three runs obtaining the same results in terms of reaction time and isolation yield of the Michael adduct **4**.

JJ-TBD **1a–d** was again much more efficient than the PS-catalysts **1e–g**, allowing a complete conversion in 100–140 min, compared to the 10 h needed for the PS-TBD **1e–g** analogues (Table 2, entries 1–4 *vs.* 5–7). Besides, the cross-linking percentage variation (Table 2, entries 2 *vs.* 4) and the mesh sizes (Table 2, entries 1–3) seem to not affect noticeably the catalytic activity, confirming thus the same trend observed in the previously illustrated Michael addition. Again, the reactions performed in the presence of an organic medium gave discouraging results (Table 2, entries 9 and 10). Obviously, PS-catalysts **1e–g** gave no trace of product in the presence of a reaction medium being always less efficient that JJ-catalysts.

Also in this case the product was isolated in very satisfactory yields (96–97%) and purities (≥ 98%).

The scope and applicability of the representative JJ-TBD catalyst **1b** has been further investigated (Table 3 and Table 4). The results are very positive confirming the efficiency of JJ-TBD as a basic catalyst. All the reactions were conducted with equimolar amounts of substrates under SolFC at 30 °C, with 0.5 mol% of catalyst (with only a few exceptions, see footnotes). The corresponding products were obtained, by simple filtration of the reaction mixture, in short times and with high yields and purities (≥ 98%).

Finally, we have evaluated the catalyst recycling. The representative base **1b** was tested in the ring opening of **5a** with **3b** in five subsequent runs on a 5 mmol scale, and we observed that its efficiency was unchanged. Product **6** was isolated in 95–97% yield after an identical reaction time (100 min). The only problem observed is related to the recovery of the solid catalyst that requires a filtration and therefore on a small scale some loss may occur.

To prove the efficiency of our approach that is based on the combination of a novel JandaJel-TBD catalyst and SolFC we have also created a continuous-flow reactor. In according with our previous reports in this field, the reactor has been designed to optimize the recovery and reuse of the catalyst, minimize waste and in particular the amount of organic solvent needed to isolate the final products.[8a–c] The schematic of the reactor is presented in Scheme 2 (thermostated box is not showed for clarity).

The equimolar mixture (50 mmol) of **5a** and **3b** was charged into a glass column functioning as a reservoir. Catalyst **1b** (0.5 mol%, 0.25 mmol of TBD) was charged into a glass column and the reaction mixture was continuously pumped through it at 30 °C for 100 min, necessary for the complete conversion to **6**.

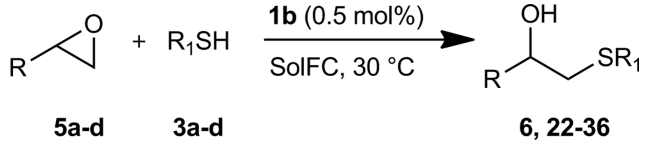
At this point, the pump was left to run in order to recover the reaction mixture into the reservoir. Then EtOAc was added (3 × 2 mL) to wash the catalyst and to isolate product **6** in 97% yield.

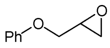
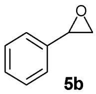
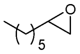
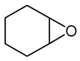
The same protocol was repeated for ten consecutive runs and the efficiency of the catalyst was unchanged. After 100 min the conversion of **5a** and **3b** to **6** was always complete and the final product was recovered always in very high yields (97–98%).

Conclusions

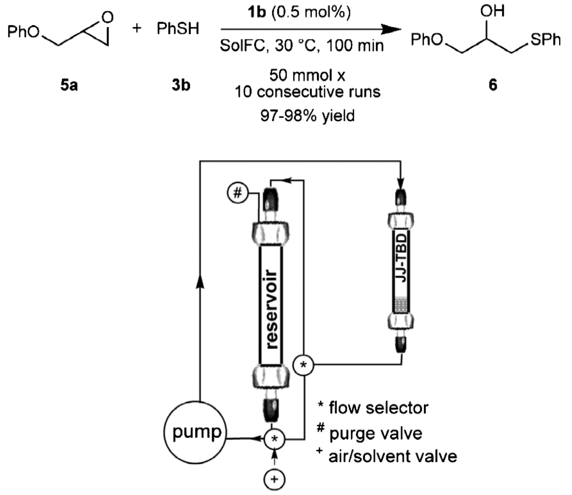
In conclusion, taking the C–S bond forming reactions of thiols **3** with Michael acceptors **2** and with epoxides **5** as purely

Table 4 Thiolysis of epoxides **5a–d** by thiols **3a–d** catalyzed by polymer-supported-TBD **1b**[a]



Entry	Epoxide	Thiol	Product	t (h)	β/α[b]	Yield[c] (%)
1	 **5a**	**3a**: *n*-BuSH	**22**	1	>99/<1	96
2		**3b**: C_6H_5SH	**6**	1.7	>99/<1	97
3		**3c**: 4-Me-C_6H_4SH	**23**	1	>99/<1	99
4		**3d**: $C_6H_5CH_2$	**24**	2	>99/<1	98
5[d]	 **5b**	**3a**	**25**	5	77/23	90
6		**3b**	**26**	7	63/37	93
7		**3c**	**27**	5	67/33	96
8		**3d**	**28**	14	66/34	94
9[e]	 **5c**	**3a**	**29**	22	>99/<1	90
10		**3b**	**30**	9	>99/<1	93
11		**3c**	**31**	8	>99/<1	96
12[d]		**3d**	**32**	9	>99/<1	90
13[e]	 **5d**	**3a**	**33**	26	—	98
14		**3b**	**34**	24	—	87
15		**3c**	**35**	30	—	88
16[e]		**3d**	**36**	1	—	85

[a] Reaction conditions: epoxide (1.0 mmol), thiol (1.0 mmol), catalyst (0.5 mol%), 30 °C. [b] Determined by GC analyses. [c] Yield of the isolated pure product. [d] 2 mol% of catalyst were used. [e] Reaction conditions: epoxide (2.0 mmol), thiol (1.0 mmol), catalyst (5 mol%), 60 °C.



Scheme 2 Schematic of the cyclic continuous-flow reactor in the reaction of **5a** and **3b** catalyzed by **1b**.

representative processes, in this communication we have showed that JandaJel resins **1a–d** ensure an excellent catalytic efficiency under SolFC compared to that of polystyrene matrices. Thanks to the greater spacing between the linear polymeric chains, reactants can access the active sites more easily without the help of a swelling medium. In addition the use of an organic medium led to a dramatic drop of the catalytic efficiency confirming our approach to the use of polymer-supported catalyst under SolFC. To optimize the recovery and reuse of the catalyst, a very efficient continuous-flow procedure operating under SolFC has been representatively realized. The results obtained prove the efficiency of this approach for realizing highly efficient processes featuring a minimal waste production.

Experimental Section

Compounds **4**,[7a] **6**,[10] **7**,[11] **8**,[12] **9**,[13] **13**,[7a] **14**,[14] **15**,[12] **16**,[15] **17**,[16] **21**,[7a] **22**,[10] **23**,[10] **24**,[17] **25** (α and β regioisomers),[18] **26** (α and β regioisomers),[19] **27** (α and β regioisomers),[20] **28** (α[21] and β[22] regioisomers), **30**,[19] **31**,[22] **32**,[23] **33**,[24] **34**,[19] **35**,[20] **36**,[25] are known and their spectroscopic data are in agreement with those reported in literature.

Compounds **10**, **11**, **12**, **18**, **19**, **20**, **29** are new compounds.

Characterization data for catalysts **1a–g**, characterization data and copies of the ^1H and ^{13}C NMR spectra for compounds **10**, **11**, **12**, **18**, **19**, **20**, **29** are in the supporting information.†

Representative experimental procedure for the synthesis of JJ-TBD catalysts. Preparation of 1a

A two-necked round-bottomed flask (25 ml) equipped with a magnetic stirrer, reflux condenser, and inert gas in- and outlet was charged with 7 ml of anhydrous THF and TBD (0.134 g, 0.96 mmol). The stirred solution was cooled to −78 °C, and *n*-BuLi in hexane (0.6 ml, 0.96 mmol) was added drop wise under nitrogen. After the addition was complete, the solution was stirred for an additional 2 h and JandaJel-Cl (200–400 mesh, 2% cross-linked, 1.163 g, 0.55 mmol(Cl) g^{-1}, 0.64 mmol) was added to the solution. The mixture was allowed to warm slowly to room temperature and stirred for 48 h under nitrogen. Then 2 ml of methanol were added to the reaction mixture, the polymer beads were isolated by filtration and washed thoroughly with THF-MeOH (1 : 1), methanol, methanol-water (1 : 1), acetone, THF, and dichloromethane. The catalyst was subsequently dried under vacuum for 15 h at room temperature and 4 h at 50 °C furnishing JJ-TBD **1a** as a yellow solid. Elemental analysis: C, 87.76; H, 7.69; N, 1.45; 0.34 mmol TBD g^{-1}.

Representative experimental procedure for the Michael addition: reaction of 1-butanethiol (3a) to (*E*)-benzylideneacetone (2a) catalyzed by polymer-supported-TBD 1b under solvent-free conditions

In a screw-capped vial equipped with a magnetic stirrer JJ-TBD **1b** (0.021 g, 0.48 mmol TBD g^{-1}, 0.01 mmol), (*E*)-benzylideneacetone (**2a**) (0.292 g, 2.0 mmol) and 1-butanethiol (**3a**) (0.215 ml, 2.0 mmol) were consecutively added and the resulting mixture was left under stirring at 30 °C. After 40 min, ethyl acetate was added, the catalyst recovered by filtration, and the organic solvent evaporated under vacuum to give ≥ 98% pure 4-(butylthio)-4-phenylbutan-2-one (**4**) as a yellowish oil (0.463 g, 98% yield).

Representative experimental procedure for the thiolysis of epoxides: reaction of 2,3-epoxypropyl-phenylether (5a) by thiophenol (3b) catalyzed by polymer-supported-TBD 1b under solvent-free conditions

In a screw-capped vial equipped with a magnetic stirrer JJ-TBD **1b** (0.031 g, 0.48 mmol TBD g^{-1}, 0.015 mmol), 2,3-epoxypropyl-phenylether (**5a**) (0.410 ml, 3.03 mmol) and thiophenol (**3b**) (0.311 ml, 3.03 mmol) were consecutively added and the resulting mixture was left under stirring at 30 °C. After 100 min, ethyl acetate was added, the catalyst recovered by filtration, and the organic solvent evaporated under vacuum to give ≥ 98% pure 1-phenoxy-3-(phenylthio)propan-2-ol (**6**) as a colourless oil (0.764 g, 97% yield).

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