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PAPER

Organocatalysis in Polysiloxane Gels: A Magnetic-Stir-Bar Encapsulated Catalyst System Prepared by Thiol-Ene Photo-Click Immobilization

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This manuscript presents a facile thiol-ene photo-click chemistry method to prepare magnetic stir bar-encapsulated polysiloxane-based organocatalyst gels under benign conditions, meanwhile develops a Stir Bar-Encapsulated Catalysis (SBEC) technique. Through thiol-ene addition chemistry, we graft olefin-terminated organocatalysts (i.e. MacMillan catalyst, Proline catalyst, and N-heterocyclic carbene catalyst) on poly[3-mercaptopropylmethylsiloxane], which is further photo-crosslinked to coat the embedded magnetic stir bar. The prepared magnetic stir bar-encapsulated polysiloxane-based organocatalyst gels can be put into reaction flasks to perform stirring and catalysis functions at the same time. The most important benefit of SBEC technique is to infinitely simplify the catalyst/product separation procedure to using a simple stir-bar-retriever, even without any precipitation/filtration steps. The catalytic performances of three different organocatalyst gels

graft olefin-terminated organocatalysts (MacMillan catalyst **C1**, Proline catalyst **C2**, and N-heterocyclic carbene (NHC) catalyst **C3**) onto PMMS chain. Meanwhile, by mixing the above systems with a photo-initiator (2,2-dimethoxy-2-phenylacetophenone, DMPA) and a variety of olefin-functional crosslinkers, a series of organocatalyst-immobilized polysiloxane gels can be synthesized by UV-initiated thiol-ene click chemistry. Compared with traditional hydrosilylation procedure, this thiol-ene photo-click protocol, as a greener and cleaner approach, has an almost 100% reaction conversion; uses cheap photo-initiators as catalysts, which are much easier to be removed; and requires very mild reaction conditions such as minute-scale reaction time, solvent-less environment-friendly process and ambient temperature, etc.

Furthermore, inspired by Stir Bar-Sorptive Extraction (SBSE) technique,[23] we use organocatalyst-immobilized PMMS gel instead of PDMS, to coat magnetic stir bar, and develop a Stir Bar-Encapsulated Catalysis (SBEC) technique. As shown in Figure 2, a plastic vial containing a magnetic stir bar and the mixture of PMMS, organocatalyst **C1**, photoinitiator DMPA and crosslinker **L3**, was UV illuminated for 20 minutes (Fig. 2A-C) to form a cross-linked gel (Fig. 2D). After breaking up the plastic vial, the prepared magnetic stir bar-encapsulated polysiloxane-based organocatalyst gel (Fig. 2E) could be put into a reaction flask to perform stirring and catalysis functions at the same time (Fig. 2F). The intrinsic motivation and the most important benefit of this approach are to infinitely simplify the catalyst/product separation procedure to using a simple stir-bar-retriever (Fig. 2G), even without any precipitation/filtration steps.

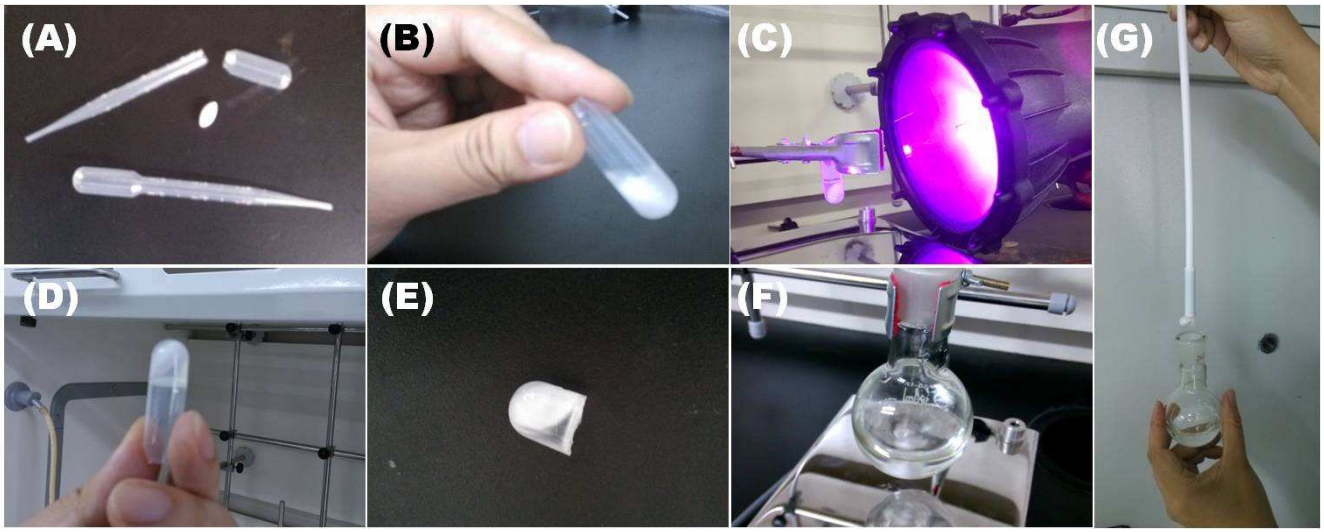


Fig. 2 Preparation protocol of magnetic stir bar-encapsulated polysiloxane-based organocatalyst gels: (A) A magnetic stir bar and plastic pipette-head vials. (B) The plastic vial was filled with a magnetic stir bar and the mixture of PMMS, organocatalyst **C1**, DMPA and crosslinker **L3**. The oily mixture was UV-illuminated (C) and became a crosslinked gel (D), which was cut out off the vial (E). (F) The obtained organocatalyst gel was performing both stirring and catalysis functions (S1.avi). (G) A stir-bar-retriever was used to separate the catalyst from products (S2.avi).

Experimental Section

Materials and Instrumentation

Poly[3-mercaptopropylmethylsiloxane] (PMMS, SMS-992, M.W. 4000~7000, 95 cst) was purchased from Gelest Inc. Poly(ethylene glycol) diacrylate (average Mn ~ 700) was purchased from Aldrich Inc. 2,2-Dimethoxy-2-phenylacetophenone (DMPA), (*s*)-phenylalanine methylester hydrochloride, allylamine, *Trans*-4-hydroxy-L-proline, undec-10-enoyl chloride, 4,5-diphenylimidazole and 11-bromo-1-undecene were purchased from Aladdin (Shanghai) Inc. Dichloromethane, toluene and DMF were distilled from CaH_2 under argon. THF was distilled from sodium-benzophenone ketyl under argon. Other chemical reagents were used without further purification. All non-aqueous reactions were conducted in oven-dried glassware, under a dry nitrogen atmosphere. All flash chromatography was performed using Macherey-Nagel MN Kieselgel 60 (0.063-1.2 mm).

All ^{1}H NMR spectra were obtained using a Bruker HW500 MHz spectrometer (AVANCE AV-500) and recorded in $CDCl_3$ (internal reference 7.26 ppm). The enantiomeric excess (ee) values were analyzed by Waters 1525 High-performance liquid chromatography (HPLC) with chiral columns. A UV lamp (20 mW·cm^{-2}, λ = 365 nm; LP-40A; LUYOR Corporation) was used to irradiate the samples to perform the photo-crosslinking reactions.

Syntheses of organocatalyst monomers C1, C2, C3. All the synthetic procedures and ^{1}H NMR spectra are listed in the supporting information.

Typical preparation procedure of stir bar-encapsulated PMMS-*g*-organocatalyst gels. In a 10 mL glass vial, PMMS (400 mg, 3.0 mmol based on -SH, 1.0 equiv.), poly(ethylene glycol) diacrylate **L3** (158 mg, 0.225 mmol, 0.075 equiv.), DMPA (15 mg), and a solution of catalyst **C1** (0.622 g, 2.55 mmol, 0.85 equiv.) in 0.2 mL CH_2Cl_2 were mixed well by centrifuge. A plastic pipette was cut off the tip, the remaining pipette head was charged with a magnetic stir bar and the above mixed solution. The pipette vial was then UV illuminated at r.t. for 20 minutes. After carefully cutting off the plastic vial by a scissor, the magnetic stir bar-encapsulated polysiloxane-based organocatalyst gel **PMMS-*g*-C1L3** was prepared. The crosslinked gel was immersed and swelled in CH_2Cl_2 several times to wash out the unreacted small molecules, and then stored in a 20 mL black glass vial with a screw cap for future uses.

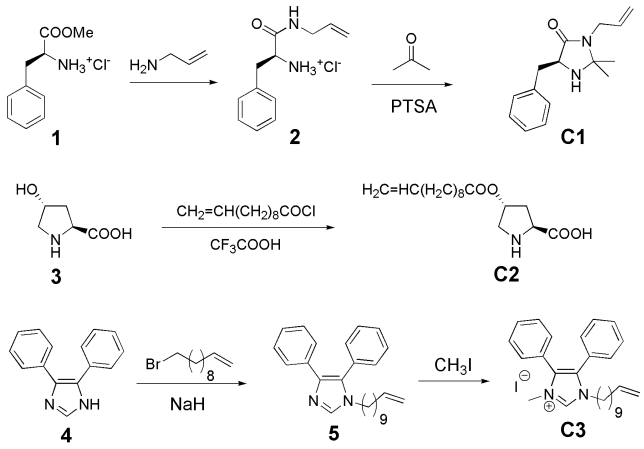
Typical synthetic procedure of asymmetric Diels-Alder reaction. In a 50 mL round-bottom flask, freshly distilled cinnamic aldehyde (0.66 g, 5.0 mmol), CH_3CN-H_2O mixture (95:5, 10 mL), stir bar-encapsulated polysiloxane-based organocatalyst gel **PMMS-*g*-C1L3** (estimated as 50 mol%, if all the grafted catalysts could be reached) and CF_3COOH (0.29 g, 2.5 mmol) were added. To the above solution freshly distilled cyclopentadiene (1.65 g, 25.0 mmol) were then added. The reaction mixture was stirred at 0 ℃ for 24 hrs. The solution was extracted by ethylacetate (3 X 50 mL). The catalyst gel **PMMS-*g*-C1L3** was removed by a stir bar retriever and immerse-washed by CH_2Cl_2 several times, stored for future uses. The resulting organic layer was washed by brine (2 X 40 mL), dried over $MgSO_4$ and was further concentrated under vacuum to provide a yellow oil. The crude product was further converted into the corresponding alcohol by reduction with an excess $NaBH_4$ in CH_3OH at 24°C for 1 hr. The endo/exo ratios were determined by crude NMR, and enantiomeric excess (ee) values were analyzed by chiral HPLC with Daciel Chiralcel OJ-H column (eluent: Hexane/isopropanol 7/3; 0.8 mL/min, λ = 225 nm).

Typical synthetic procedure of asymmetric aldol reaction. In a 50 mL round-bottom flask, 4-nitrobenzaldehyde (0.50 g, 3.29 mmol), cyclohexanone (2.23 g, 23.0 mmol), H_2O (10 mL) and stir bar-encapsulated polysiloxane-based organocatalyst gel **PMMS-*g*-C2L3** (estimated as 77 mol%, if all the grafted catalysts could be used) were added. The reaction mixture was stirred at 50 ℃ for 48 hrs. The solution was extracted by ethylacetate (3 X 50 mL). The catalyst gel **PMMS-*g*-C2L3** was removed by a stir bar retriever and immerse-washed by CH_2Cl_2 several times, stored for future uses. The resulting organic layer was washed by brine (2 X 40 mL), dried over $MgSO_4$ and was further concentrated under vacuum to provide a yellow oil, which was purified by flash column chromatography (10:1 petroleum ether - ethylacetate) to give the desired product as a yellow solid. The anti/syn ratios and enantiomeric excess (ee) values were analyzed by chiral HPLC with Daciel Chiralpak AD-H column (eluent: isohexane/isopropanol 9/1; 1.0 mL/min, λ = 254 nm).

Typical synthetic procedure of benzoin condensation reaction. In a 50 mL round-bottom flask, benzaldehyde (0.78 g, 7.4 mmol), DMSO (10 mL), DBU (0.168 g, 1.1 mmol) and stir bar-encapsulated polysiloxane-based organocatalyst gel **PMMS-*g*-C3L3** (estimated as 34 mol%, if all the grafted catalysts could be used) were added. Under nitrogen atmosphere, the reaction mixture was stirred at 25 ℃ for 48 hrs. The solution was extracted by ethylacetate (3 X 50 mL). The catalyst gel **PMMS-*g*-C2L3** was removed by a stir bar retriever, regenerated by a solution of 4.0 M HCl in 1,4-dioxane, immerse-washed by CH_2Cl_2 several times, and stored for future uses. The resulting organic layer was washed by brine (2 X 40 mL), dried over $MgSO_4$ and was further concentrated under vacuum to provide a crude oil, which was purified by flash column chromatography (10:1 petroleum ether - ethylacetate) to give the desired benzoin product (490 mg, Yield: 63%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (m, 2H), 7.51 (m, 1H), 7.39 (m, 2H), 7.30 (m, 5H), 5.95 (s, 1H).

Results and Discussion

The synthetic protocols of olefin-terminated organocatalyst monomers including MacMillan catalyst **C1**, Proline catalyst **C2**, and NHC catalyst **C3** are shown in Scheme 1. The ester-amide exchange of (*S*)-phenylalanine methyl ester hydrochloride with allyl amine, followed by condensation reaction with acetone gave the imidazolinone catalyst **C1**.[24] Proline catalyst **C2** was prepared by a selective *O*-acylation of *trans*-4-hydroxy-L-proline **3** in trifluoroacetic acid.[25] Starting from 4,5-diphenylimidazole **4**, NHC catalyst **C3** was synthesized in two steps by alkylation with 11-bromo-1-undecene and further quaterisation treatment with iodomethane.[26] The detailed experimental procedures and ^{1}H NMR spectra are listed in the supporting information.



Scheme 1 Syntheses of olefin-terminated MacMillan catalyst, Proline catalyst, and NHC catalyst.

For preparing magnetic stir bar-encapsulated polysiloxane-based organocatalyst gels, efficient crosslinkage based on the design of crosslinker and crosslinking ratio plays a crucial role in building a stable polymeric network. Based on our previous experiments, commercial PMMS are short oligomers with an estimated degree of polymerization (D.P.) around 30.[27,28] Thus, in order to form a stable cross-linked PMMS gel, the molar percentage of the crosslinking sites should be at least higher than 7-8 mol% and herein we set 15 mol% as a constant crosslinking ratio for all the experiments. Three crosslinkers, triallyl cyanurate (**L1**, TAC), 1,6-hexanediol diacrylate (**L2**), poly(ethylene glycol) diacrylate (**L3**, average Mn ~ 700) were tested in the experiments respectively. In comparison, although all three crosslinkers could be successfully used to synthesize polysiloxane gels, the gels containing a much longer and flexible crosslinker, poly(ethylene glycol) diacrylate are more elastic and stable than other brittle gels prepared by triallyl cyanurate or 1,6-hexanediol diacrylate crosslinkers.

As shown in Figure 2, before UV illumination, we first dissolved an organocatalyst into a small amount of methylene chloride which was then mixed with PMMS, photoinitiator and crosslinker to form an oily liquid. The mixture was then poured into a vial containing a magnetic stir bar. Herein, we chose a soft plastic container (PE pipette head, Fig. 2A) in stead of glass vials, because compared with scissor-cut plastic pieces, shattered glass would easily damage the prepared gels in the last step. After UV illumination, the oily liquid became a crosslinked gel (Fig. 2D), which was cut out of the plastic vial and immersed in dry methylene chloride several times to wash out unreacted small molecules. The desired magnetic stir bar-encapsulated

polysiloxane-based organocatalyst gel was prepared. However, our prototype manufacturing system has two technique problems: 1) magnetic stir bars are randomly embedded in PMMS gels and we can not precisely arrange the locations and postures of stir bars placed in the gels. Thus, the prepared organocatalyst gels will have physically vulnerable points where the stir bars touch on the walls of plastic container, and this imperfectness results in a moderate stirring effect (see the stirring movie, SI1.avi). 2) The organocatalyst gels are partially crosslinked and would be better to be stored in organic solvents to maintain elasticity. For example, we have tried to remove all the solvent from the gels *via* vacuum, which unfortunately caused the spontaneous fission of gels.

Although some flaws exist in our prototype products at present, future industrial manufacturing can be expected to realize technique improvements. Herein, we prepared three magnetic-stir-bar-encapsulated organocatalyst gels, **PMMS-*g*-C1L3**, **PMMS-*g*-C2L3** and **PMMS-*g*-C3L3**, which were used in catalyzing asymmetric Diels-Alder reaction, asymmetric aldol reaction and benzoin condensation reaction respectively.

The imidazolidinone compound developed by MacMillan,[29] might be the most famous organocatalyst which has been widely used in a variety of organocatalytic processes and has been unsurprisingly immobilized on different polymeric supports.[24,25,30-34] Polysiloxane gel catalyst, **PMMS-*g*-C1L3** bearing MacMillan imidazolidinone was applied to promote a classical asymmetric Diels-Alder reaction of cyclopentadiene and cinnamic aldehyde.

Table 1 Enantioselective Diels-Alder reaction catalyzed by catalyst **PMMS-*g*-C1L3**

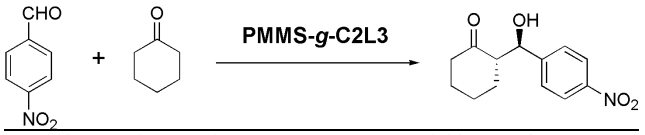
Entry[a]	Recycle number	Acid	Solvent	Yield (%)[b]	exo/endo (%)[c]	exo ee (endo ee) (%)[d]
1	0	HBF_4	CH_3CN/H_2O (95/5)	0	--	--
2	0	TFA	$MeOH/H_2O$ (95/5)	52	51/49	66 (83)
3	0	TFA	CH_3CN/H_2O (95/5)	88	51/49	78 (96)
4	1	TFA	CH_3CN/H_2O (95/5)	73	55/45	77 (77)
5	2	TFA	CH_3CN/H_2O (95/5)	66	53/47	78 (79)
6	3	TFA	CH_3CN/H_2O (95/5)	74	51/49	74 (77)
7	4	TFA	CH_3CN/H_2O (95/5)	72	51/49	73 (72)
8	5	TFA	CH_3CN/H_2O (95/5)	64	54/46	70 (79)

[a] Reactions were carried out using cinnamic aldehyde (1 equiv.) and cyclopentadiene (5 equiv.) at 0 ℃ for 24 hrs. [b] Isolated yield. [c] Determined by crude NMR. [d] Determined by chiral HPLC.

As shown in Table 1, roughly 50 % : 50 % mixture of *endo* and *exo* cycloadducts (determined by ^1H NMR analysis of crude products) were isolated in all the experimental trials. To convert the grafted imidazolidinone **C1** to the catalytically active intermediate, an equimolar amount of a Bronsted acid is required to protonate the supported organocatalyst. Traditionally, HBF_4 has been proven to be a very efficient acid in this reaction system,[24] however in our case, this choice provided negative results (Entry 1), possibly due to the strong lewis acidity and F^- ion of HBF_4 which might be able to destroy C-S-C and Si-O bonds. The alternative use of trifluoroacetic acid in acetonitrile/water (95/5) solvent provided an optimal 88% yield with moderate *endo* (96%) and *exo* (78%) ee values (Entry 3). The recovered **PMMS-*g*-C1L3** gel was recycled five times to test the catalytic performances. As can be seen from the reported data (Entry 4-8), the conversion efficiency and catalyst stereoselectivity were maintained at around 70% reaction yield and 77% ee, although slightly lower than the first trial's result. Nonetheless, **PMMS-*g*-C1L3** gel can be conveniently employed to catalyze asymmetric Diels-Alder cycloadditions.

Polymer-supported L-proline represents another very important class of organocatalysts for C−C bond constructions such as asymmetric aldol reaction.[25,35-46] Following literature protocols, we tested the catalytic performance of polysiloxane gel **PMMS-*g*-C2L3** applied in a classical enantioselective aldol reaction of 4-nitrobenzaldehyde and cyclohexanone. As illustrated in Table 2, solvent plays a crucial role in enantioselective property. The reaction carried out in methanol/H_2O (1/1, v/v) system provided moderate yields and low ee (34-38%), while using pure water solution resulted in high conversion (> 80%) and high ee values (96-99%). Unlike traditional homogeneous reactions which would have a significant decrease in both stereo- and enantioselectivity along with raising reaction temperature,[47-50] our **PMMS-*g*-C2L3** catalyst gel slightly favors higher temperature possibly due to the hydrophobicity of polysiloxanes expelling water from catalytic centers to stabilize the transition state of forming enamine species by excluding competitive hydrogen bonding with water. This phenomena is consistent with Monteiro's observation.[46]

Table 2 Enantioselective aldol reaction catalyzed by catalyst **PMMS-*g*-C2L3**



Entry[a]	Recycle number	Solvent	Temperature (℃)	Yield (%)[c]	*anti/syn* (%)[d]	*anti* ee (%)[e]
1	0	$MeOH/H_2O$ (1/1)	25	68	89/11	38
2	0	$MeOH/H_2O$ (1/1)	50	65	92/8	34
3	0	H_2O	25	80	88/12	90
4[b]	0	H_2O	50	82	88/12	96
5	0	H_2O	50	85	90/10	99
6	1	H_2O	50	87	86/14	91
7	2	H_2O	50	76	90/10	72
8	3	H_2O	50	75	81/19	60
9	4	H_2O	50	69	85/15	24
10	5	H_2O	50	73	56/44	22

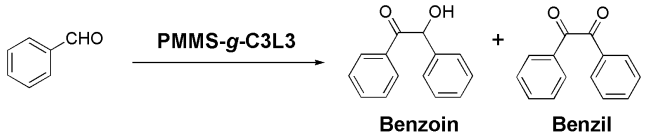
[a] Reactions were carried out using 4-nitrobenzaldehyde (1 equiv.) and cyclohexanone (7 equiv.) for 48 hrs. [b] Catalyst: **PMMS-*g*-C2L2**. [c] Iolated yield. [d] Determined by chiral HPLC. [e] Determined by chiral HPLC.

The recovered **PMMS-*g*-C2L3** gel was reused five times to test the recyclability of catalyzing the asymmetric aldol reaction. As shown in Table 2, the first two runs provided satisfying

reaction yields and high ee values (entry 5-6), however the enantioselectivity decreased dramatically starting from the third recycle (entry 7-10). Besides the lack of exploration in optimal reaction conditions, one possible reason might be that since the recovered **PMMS-*g*-C2L3** gel was always kept in solvents to avoid gel fission, some leftover chemicals might "poison" or racemize the grafted L-Proline catalyst.

Incorporating imidazolium salts into the polymer backbones or side chains has been proven to be an efficient way to develop recyclable polymeric NHC catalysts.[26,51-58] Inspired from Cowley's work,[26] we designed and synthesized an imidazolium monomer **C3**, and grafted it onto crosslinked PMMS gels. With **PMMS-*g*-C3L3** catalyst in hand, we examined its ability of catalyzing a typical benzoin condensation reaction.

Table 3 Benzoin condensation reaction catalyzed by catalyst **PMMS-*g*-C3L3**



Entry[a]

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