Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Electronic Supplementary Information
for
Ionic liquid-derived polyelectrolyte promoting the biphasic condensation of immiscible reactants at moderate temperature

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1. Materials and Instrumentation

1-Methylimidazole and Amberlyst® 15 hydrogen form were purchased from Sigma-Aldrich Chemical Co. Tri-*n*-octylphosphine, 1,4-butanesultone, oleic acid (OA), divinylbenzene (DVB), trifluoroacetic acid (TFA), *p*-toluenesulfonic acid monohydrate, and 2,2'-Azobis(isobutyronitrile) (AIBN) were purchased from Tokyo Chemical Industry Co. Bis(trifluoromethanesulfonyl)imide (H[Tf_2N]) was purchased from Kanto Chemical Co. Glycerol (Gly) and hydrochloric acid (1 mol/L) were purchased from FUJIFILM Wako Pure Chemical Co. Sodium 4-styrenesulfonyl(trifluoromethanesulfonyl)imide (Na[TfNS]) was purchased from Tosoh Finechem Co. 1-Methylimidazole was distilled prior to the synthesis, and other chemicals and solvents were used as received. Elemental analysis of the prepared PILC1 was performed with a vario MICRO cube (Elementar) instrument. Optical microscopy studies were performed with an OLYMPUS BX 51 system. Chromatographic analysis was performed with ACQUITY UPLC H-Class system (Waters).

2. Synthesis of ILCs

The ILCs used in this study (ILC1 and ILC2) were prepared according to the literature reported.[1] For ILC1, tri-*n*-octylphosphine and 1,4-butanesultone were mixed in toluene at a 1.0/1.1 molar ratio, and the solution was refluxed for 3 days. After evaporation of the solvent, the product was washed with diethyl ether for several times. The resulting solid was dried *in vacuo* to obtain a zwitterionic precursor, 4-(tri-*n*-octylphosphonio)butanesulfonate ($P_{8884}SO_3$). The precursor was mixed with an equimolar amount of H[Tf_2N] in dry methanol while cooling the solution in an ice bath. A homogeneous solution was obtained after stirring the solution for a couple of hours. Methanol was evaporated, and the resulting liquid was dried *in vacuo* at 50 °C for at least 48 h to obtain ILC1 ([$P_{8884}SO_3H$][Tf_2N]) as a colourless liquid. For ILC2 ([$Im_{14}SO_3H$][Tf_2N]), a zwitterionic precursor, 4-(1-methyl-3-imidazolium-3-yl)butanesulfonate ($Im_{14}SO_3$), was prepared by mixing 1-methylimidazole and 1,4-butanesulfonate in acetonitrile and refluxing for 24h. Subsequent procedure was the same as that for preparing ILC1.

ILC1. ^1H NMR (400 MHz, $CDCl_3$, δ/ppm): 0.90 (t, J = 8.4 Hz, 9H), 1.30 (br, 24H), 1.49 (br, 12H), 1.76 (br, 2H), 2.06 (br, 8H), 2.22 (t, J = 21.0 Hz, 2H), 3.22 (t, J = 10.5 Hz, 2H), 10.3 (br).

^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 13.97, 18.32, 18.78, 19.82 (d, J = 3.0 Hz), 21.44 (d, J = 4.0 Hz), 22.53, 24.63 (d, J = 17.0 Hz), 28.65, 28.87, 30.53 (d, J = 14.0 Hz), 31.61, 50.45, 119.74 (q, J = 319.3 Hz).

ILC2. ^{1}H NMR (400 MHz, D_2O, δ/ppm): 1.64-1.72 (m, 2H), 1.91-1.99 (m, 2H), 2.87 (t, J = 11.1 Hz, 2H), 3.82 (s, 3H), 4.16 (t, J = 10.5 Hz, 2H), 7.36 (s, 1H), 7.42 (s, 1H), 8.64 (s, 1H). ^{13}C NMR (100 MHz, D_2O, δ/ppm): 20.95, 28.11, 35.64, 48.92, 50.07, 119.26 (q, J = 318.0 Hz), 122.18, 123.67, 135.87.

3. Synthesis of PILC1

To a Schlenk flask with a greaseless stopcock and a stir bar, Na[TfNS] (0.34 g, 1 mmol), $P_{8884}SO_3$ (0.51 g 1 mmol), DVB (1.30 g, 10 mmol), AIBN (34.5 mg, 0.21 mmol), ultrapure water (4.0 ml), and tetrahydrofuran (1.0 ml) were added and degassed by three freeze-pump-thaw cycles. The flask was then warmed to 25 °C and filled with N_2 gas. The resulting mixture was heated at 60 °C and stirred for 3h. After cooling the mixture to room temperature, 1 mol/L hydrochloric acid (20 ml) was poured in the mixture and stirred for 24h to exchange Na^+ to H^+. The product was then filtered and washed with water and hexanes, dried *in vacuo* at 80 °C to give cross-linked PILC1 as a white powder. The above synthetic procedure was undertaken for three times, and the chemical composition of each sample was characterised by elemental analysis (Table S1). The best fit for the chemical composition of the resulting compound was poly($[P_{8884}SO_3H][TfNS]_1$-*co*-$DVB_{7\text{-}8}$).

4. Product analysis for the esterification of Gly and OA

The products and the unreacted OA were analysed by UPLC with refractive index (RI) detector. The chromatography was performed with an AQUITY UPLC HSS T3 column (2.1 × 100 mm, 1.8 μm particle size) and a mobile phase consisting of acetone:acetonitrile:TFA (60:40:0.1 v/v/v) through an isocratic mode. The temperatures of the column and RI detector were set at 40 °C.

5. Reusability of PILC1

The esterification of Gly with OA in the presence of PILC1 was performed according to the same procedure in Table 1. After the reaction, PILC1 was washed with hexane and water for several times, filtered, and dried *in vacuo* at 60 °C. The collected PILC1 was reused for the second reaction.

Supporting Tables and Figures

Table S1 Elemental analysis of PILC1

	x:y^a	C(%)		H(%)		N(%)		S(%)	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Sample 1	1:7	74.14	73.07	7.97	8.60	0.81	0.81	5.55	5.29
Sample 2	1:8	75.41	74.99	7.95	8.77	0.75	0.67	5.16	4.04
Sample 3	1:8	75.41	75.19	7.95	8.87	0.75	0.51	5.16	4.11

$^a x$ and y respectively denote the chemical composition of $[P_{8884}SO_3H][TfNS]$ and DVB.

Table S2 Reusability of PILC1 to produce glyceryl oleate

	Conversion of OA/%	Yield of esters/%	Selectivity/%		
			Monoester	Diester	Triester
1st run	41.13 ± 5.5	39.7 ± 1.6	81.8 ± 3.7	17.9 ± 3.7	0.3 ± 0.1
2nd run	47.0 ± 5.0	39.5 ± 3.5	78.5 ± 0.5	21.1 ± 0.5	0.4 ± 0.1

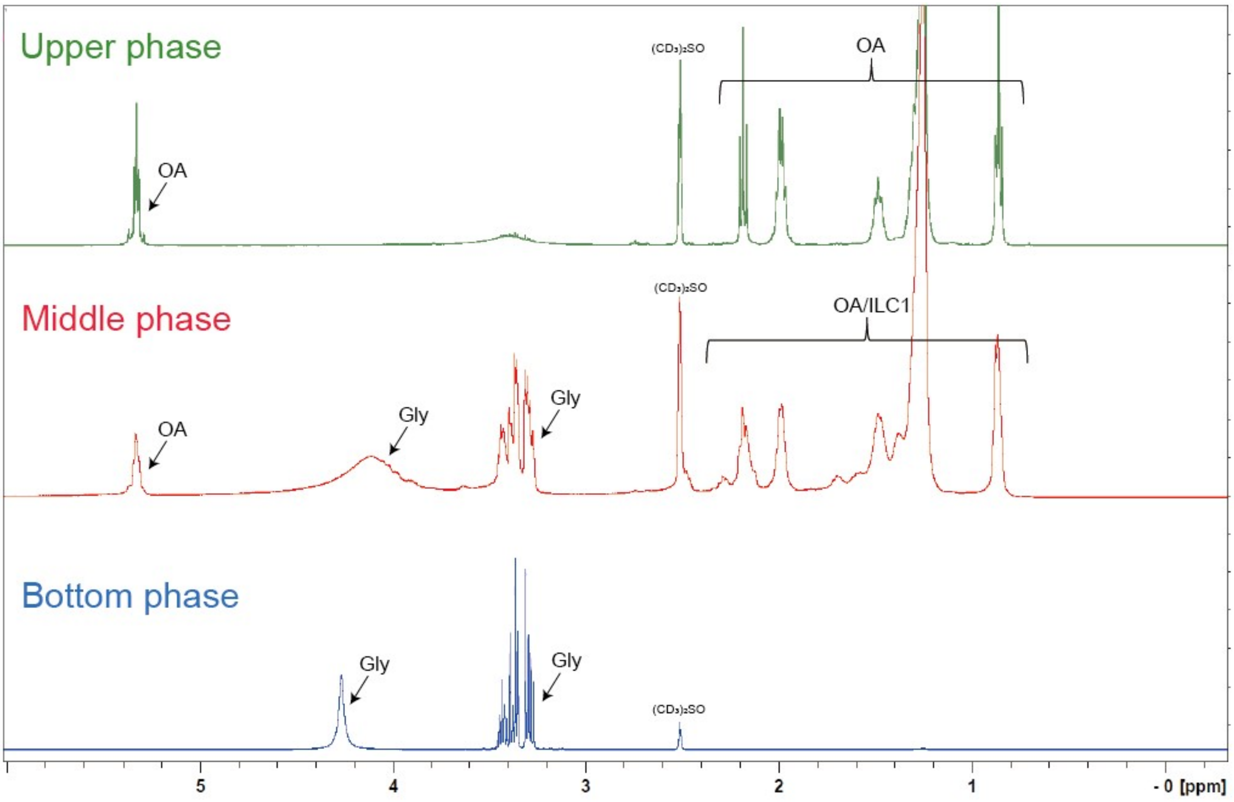


Fig. S1 ^{1}H NMR spectra of upper phase (green line), middle phase (red line), and bottom phase (blue line) for OA/ILC1/Gly triphasic system.

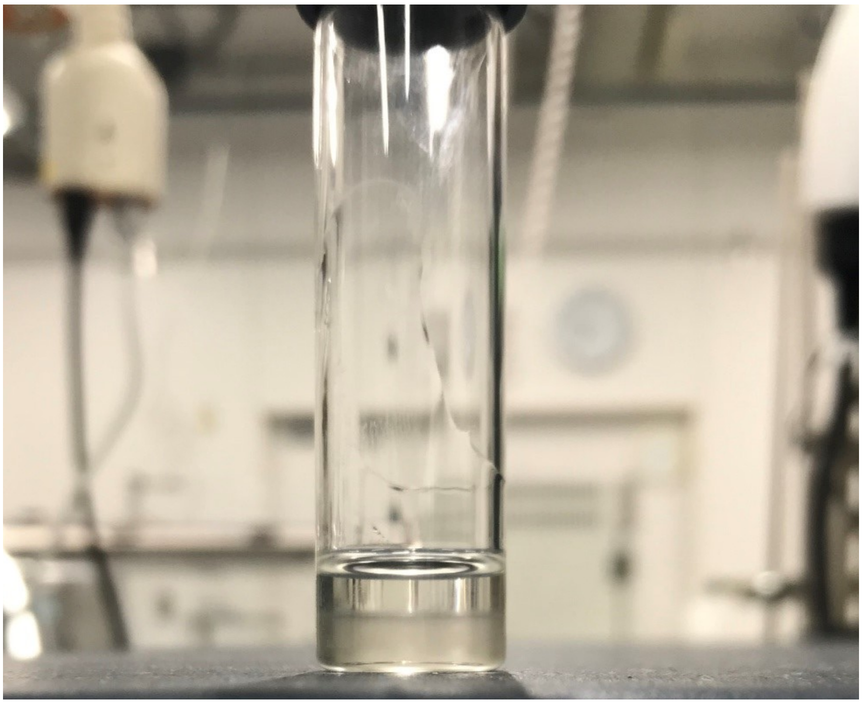


Fig. S2 Photograph showing biphasic phase behaviour of OA/ILC2/Gly.

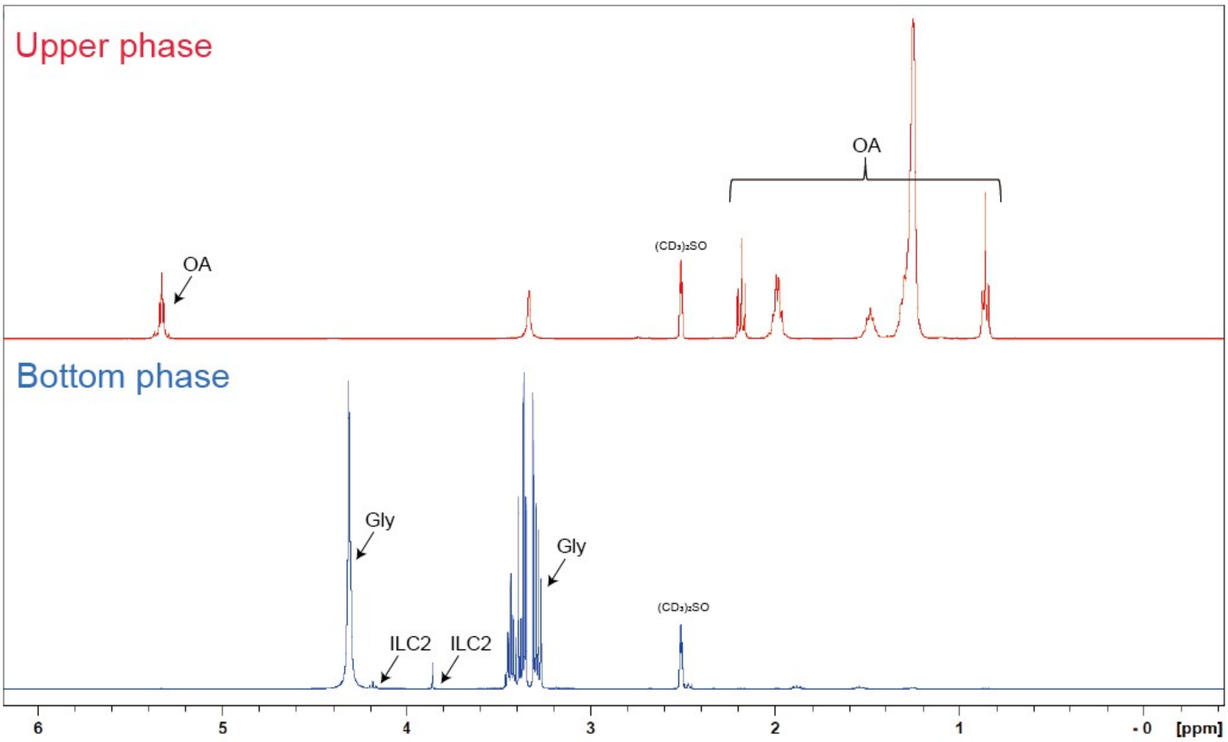


Fig. S3 ^{1}H NMR spectra of upper phase (red line) and bottom phase (blue line) for OA/ILC2/Gly biphasic system.

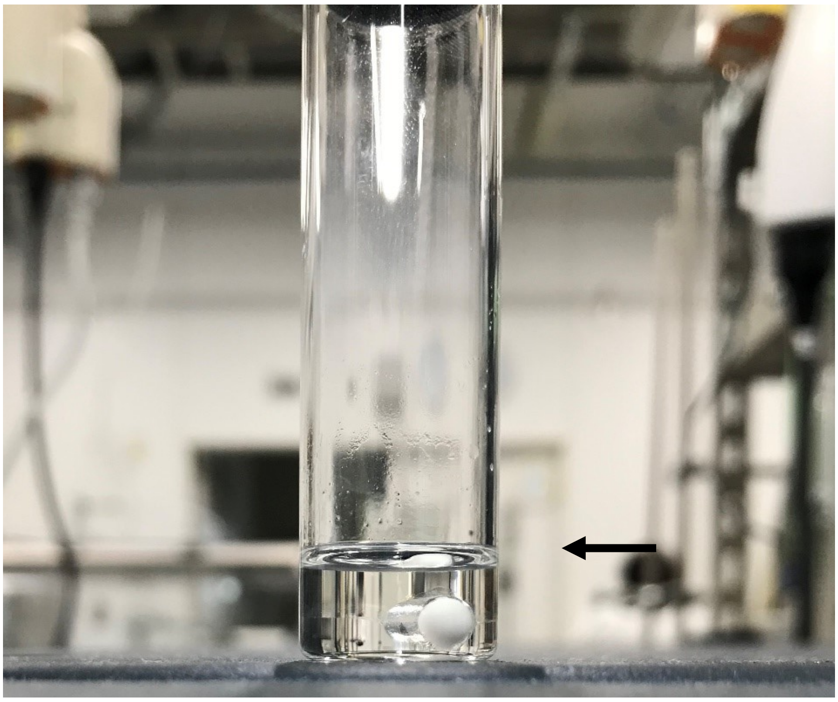


Fig. S4 Photograph showing a reaction mixture of OA/Gly/ILC1 after stirring at 60 °C for 6h and storing until the phases became clear. The black arrow denotes the liquid-liquid interface.

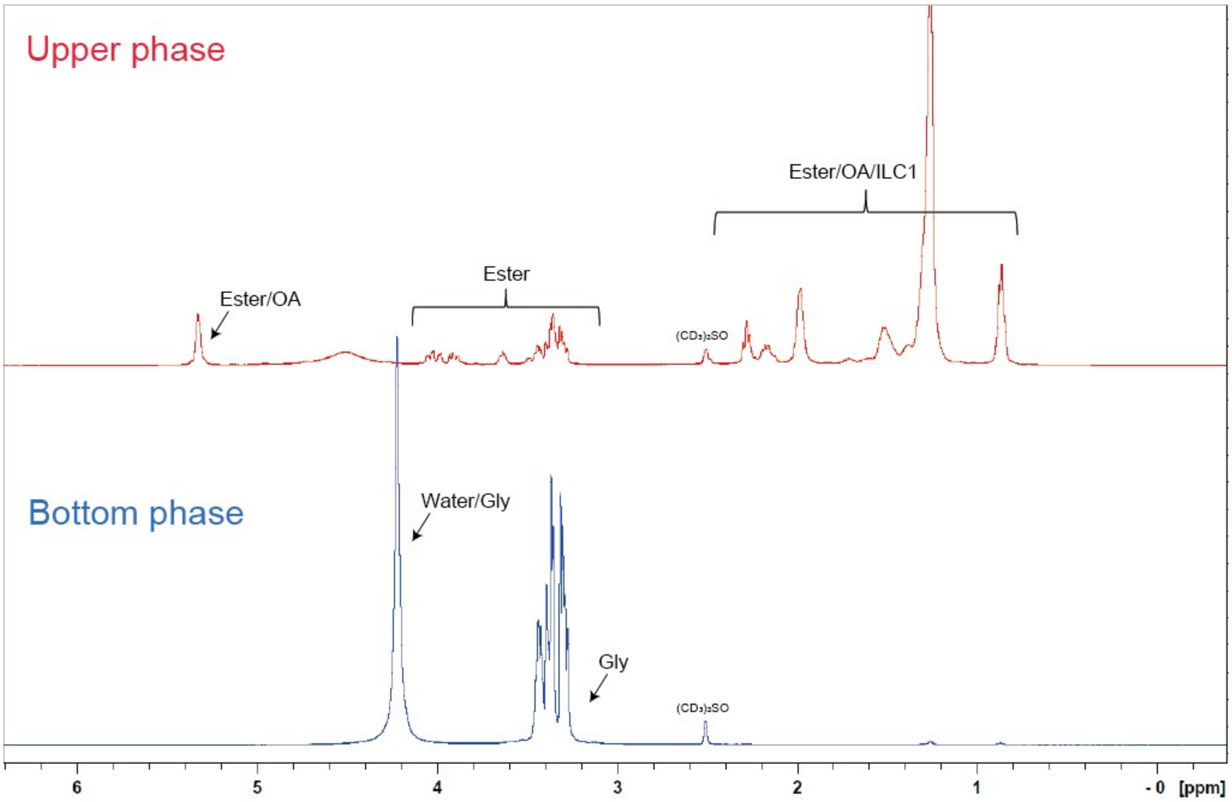
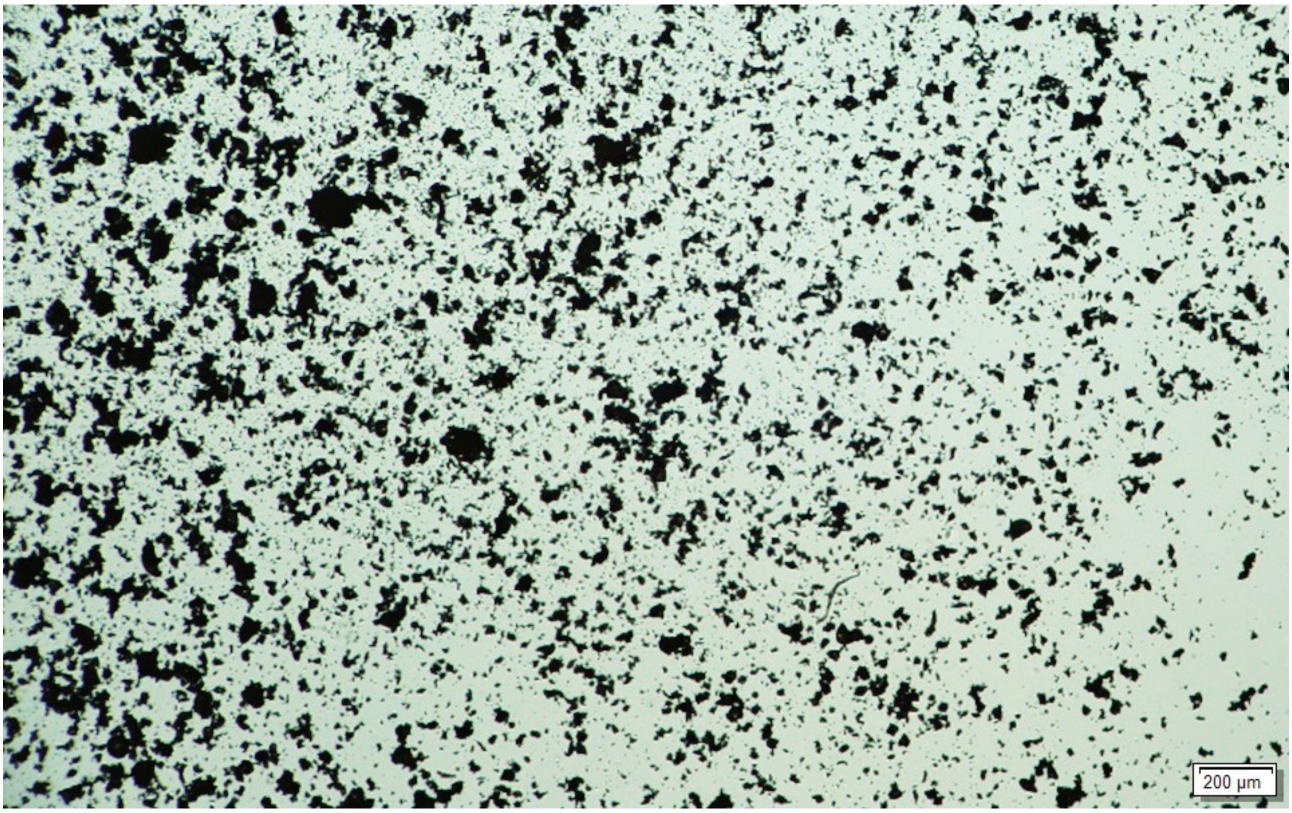


Fig. S5 ^{1}H NMR spectra of upper phase (red line) and bottom phase (blue line) after the esterification of Gly and OA in the presence of ILC1. The amount of water by-product in the bottom phase was calculated to be 96%, from the integral of water peak in the bottom phase.



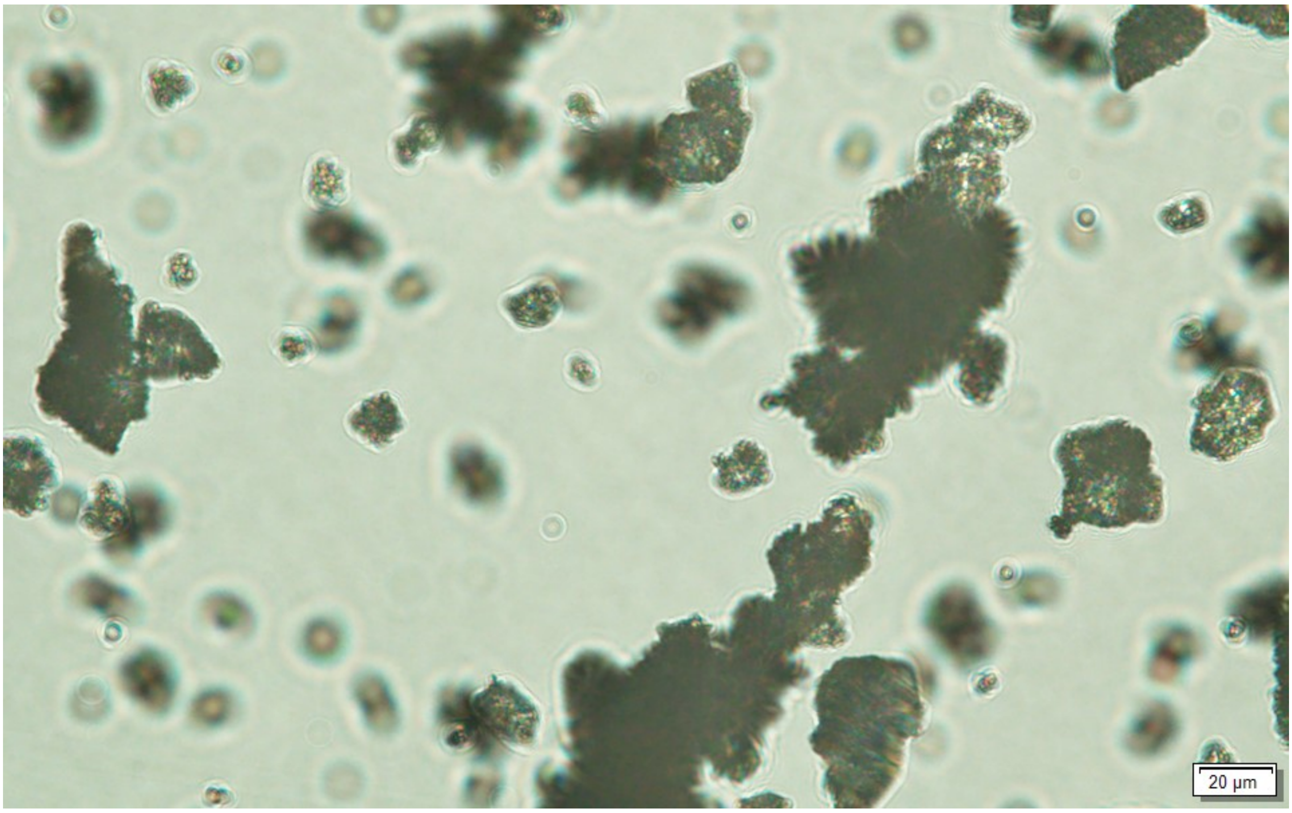


Fig. S6 Microscopy images of PILC1.

Reference for the ESI

1 Y. Kohno, T. Makino and M. Kanakubo, *React. Chem. Eng.*, 2019, **4**, 627.