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Two-dimensional zeolitic imidazolate framework ZIF-L: A promising catalyst for polymerization

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Abstract: Here, for the first time, a 2D and leaf-like zeolitic imidazolate framework (ZIF-L) is reported for the synthesis of ultrahigh molecular weight (UHMW) poly(methyl methacrylate) (PMMA) with M_n up to 1390 kg mol^{-1}. This synthesis method is a one-step process without any co-catalyst in a solvent-free medium. SEM, PXRD, FT-IR, TGA, and nitrogen sorption measurements confirmed the 2D and leaf-like structure of ZIF-L. The results of PXRD, SEM, TGA demonstrate that the catalyst ZIF-L is remarkably stable even after a long-time polymerization reaction. Zwitterionic Lewis pair polymerization (LPP) has been proposed for the catalytic performance of ZIF-L on methyl methacrylate (MMA) polymerization. This MMA polymerization is consistent with a living system, where ZIF-L could reinitiate the polymerization and propagates the process by gradually growing the polymer chains.

Keywords: Ultrahigh molecular weight polymer; Poly methyl methacrylate; heterogeneous catalyst; Zeolitic imidozolate framework.

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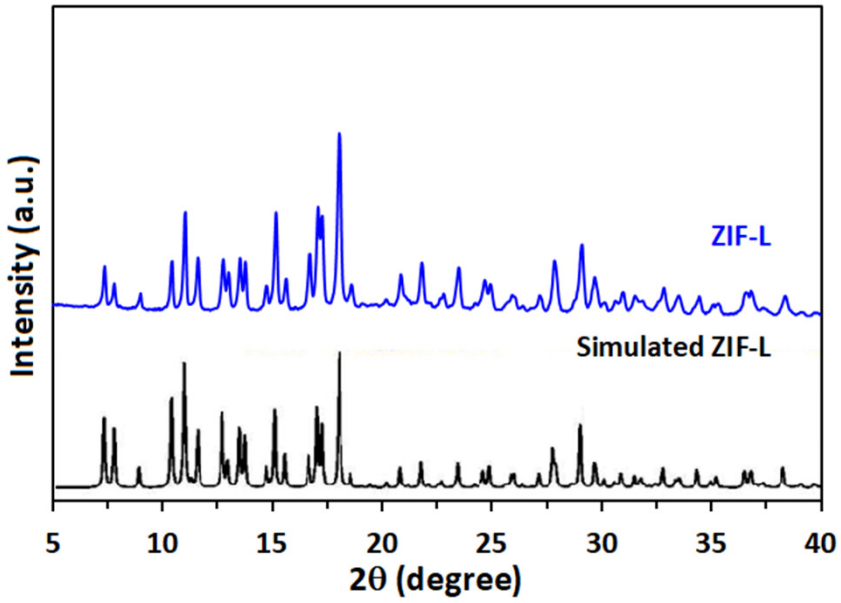

Figure S1. PXRD patterns of the synthesized and simulated ZIF-L (Zn).[1,2].

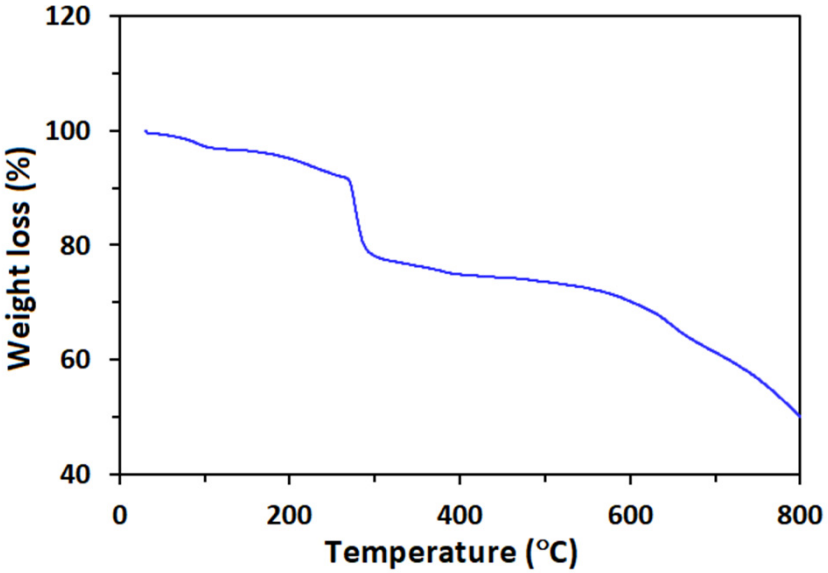

Figure S2. TGA curve of ZIF-L under N_2 flow (20 mL/min) ranging from 30 °C to 800 °C.[3,4].

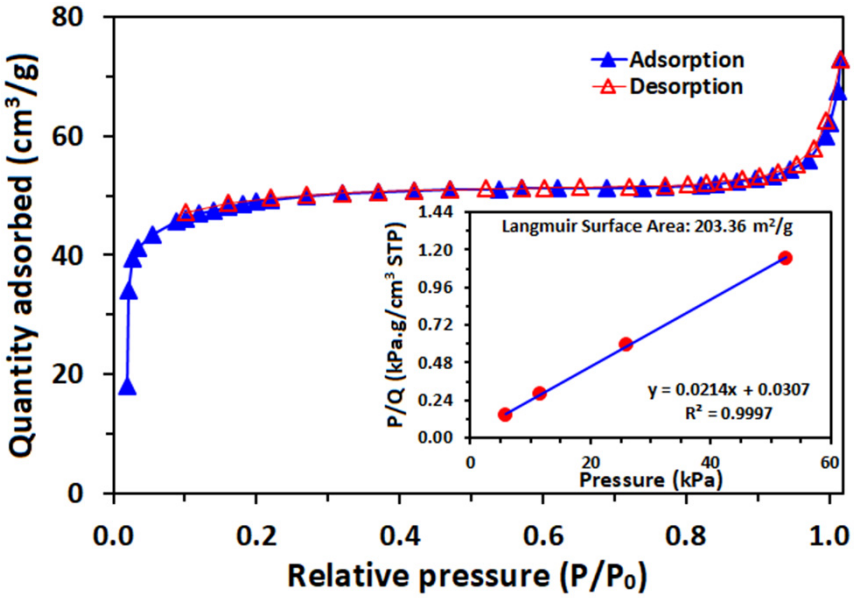

Figure S3. The isotherms of nitrogen adsorption (filled symbols) and desorption (empty symbols) for the ZIF-L measured at -196 °C.

Table S1. Bulk polymerization of MMA initiated with various Zn-salts, 2-mIm (ligand used for ZIF-L synthesis) and ZIF-L [a].

entry	catalyst	conv.[b] (%)	M_n [c] (kg/mol)	$Đ$[c]
1	no catalyst	-	-	-
2	$Zn(NO_3)_2{\cdot}6H_2O$	71	130	1.97
3	2-mIm	31	367	1.82
4	ZnO	85	380	1.49
5	$Zn(OAc)_2.\ 2H_2O$	88	429	1.42
6	ZIF-L	83	1390	1.12

[a] Reaction conditions: [MMA]/[catalyst] = 50; temperature = 140 C; time = 24 h, b determined by 1H NMR spectroscopy in CDCl3, c determined by GPC analysis in THF at room temperature referenced to polystyrene standards.

Table S2. Amount of acid and basic sites of the catalyst (ZIF-L).

Sample	NH_3-TPD		CO_2-TPD	
	Weak acid	Strong acid	Weak base	Strong base
ZIF-L	2.80 mmol/g	4.29 mmol/g	0.02 mmol/g	0.91 mmol/g
	240 – 470 °C	480 – 690 °C	220 – 295 °C	295 – 765 °C

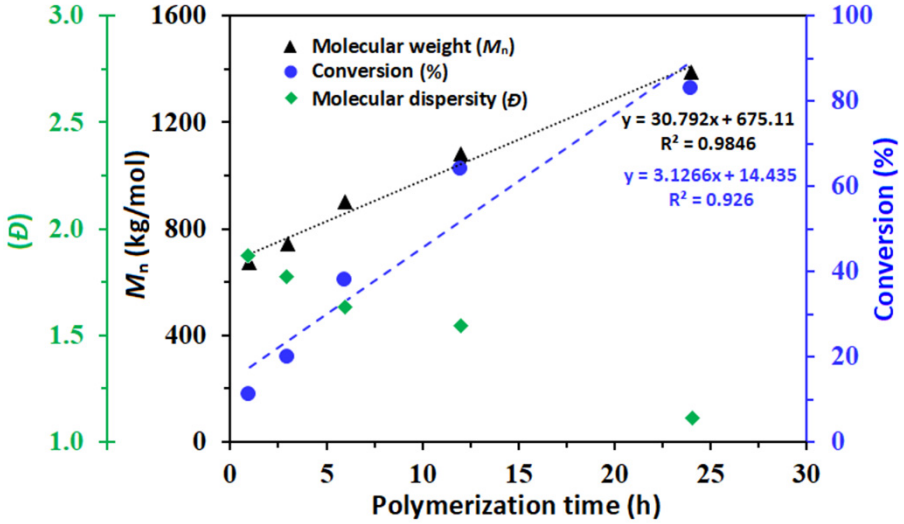

Figure S4. Dependence of molecular weight (M_n), monomer conversion (%) and molecular dispersity ($Đ$) on polymerization time (h) for MMA polymerization using ZIF-L(Zn).

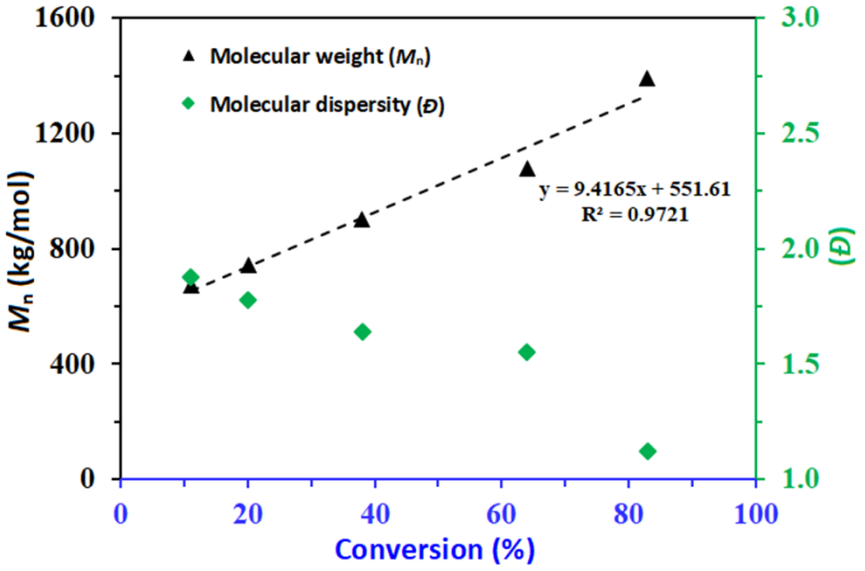

Figure S5. Dependence of molecular weight (M_n) and molecular dispersity (Đ) on monomer conversion (%) for MMA polymerization using ZIF-L.

Table S3. Chain-extension experiments of the polymerization of MMA at 140 °C.

entry	[MMA]/[ZIF-L]	time (h)	conv.[a] (%)	M_n [b] (kg/mol)	$Đ$[b]
run 1	200/1	55	> 90	1514	1.11
run 2	run 1 + 200 equivalent MMA	55 + 60	> 90	2843	1.24

[a]conv. = % of MMA conversion calculated by ^{1}H NMR integration of the methoxy resonance relative intensities of the residual MMA and PMMA in $CDCl_3$, [b]Determined by gel permeation chromatography (GPC) analysis in THF at RT referenced to polystyrene standards.

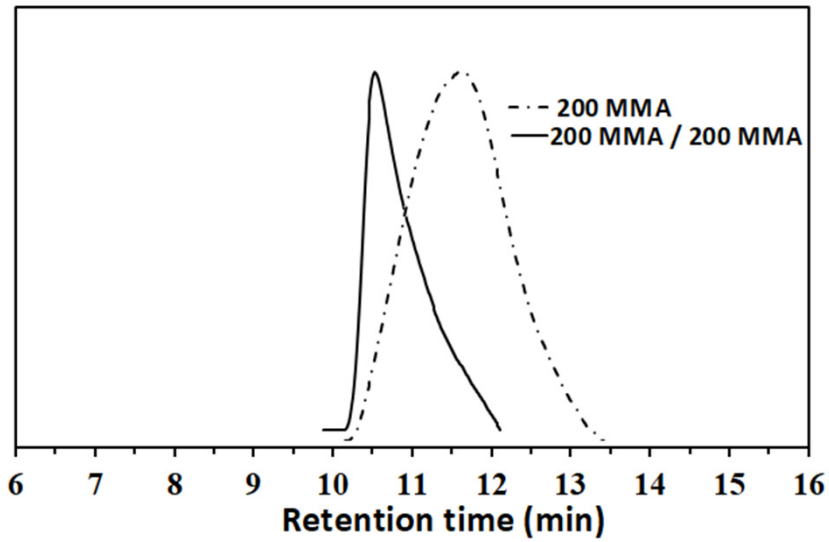

Figure S6. GPC traces of PMMA obtained from chain extension experiments.

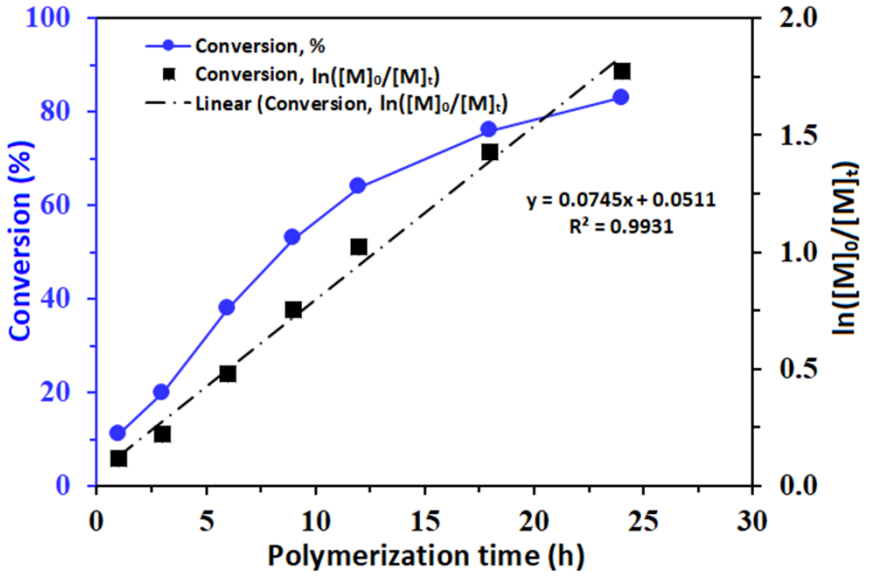

Figure S7. MMA conversion with polymerization time initiated by ZIF-L at 140 °C and [MMA]/[ZIF-L] = 50.

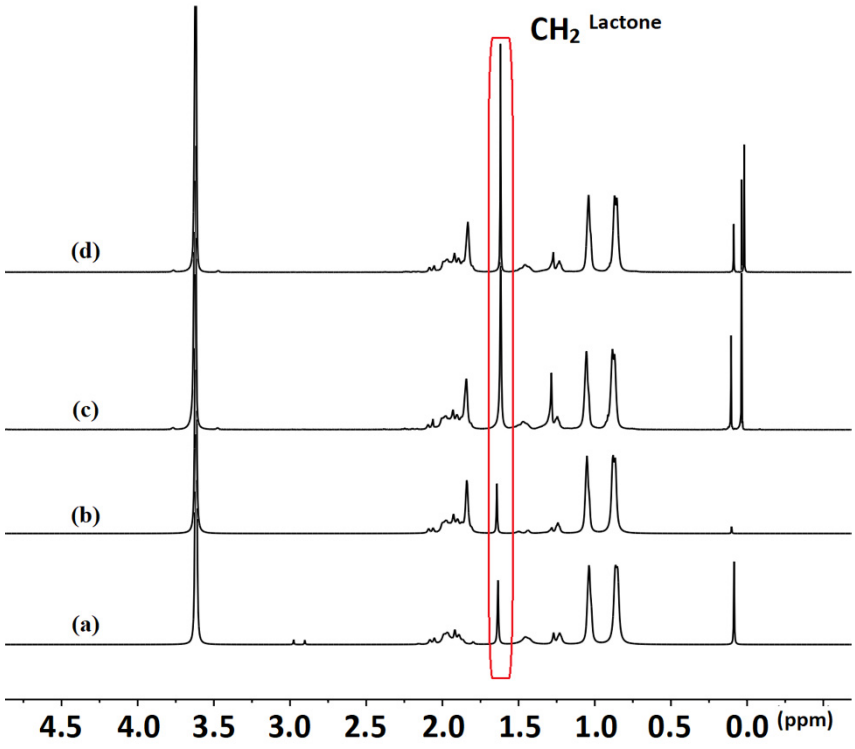

Figure S8. ^{1}H-NMR spectra of (a) ZIF-L, (b) 2-mIm, (c) $Zn(OAc)_2$ and (d) ZnO mediated PMMA in $CDCl_3$ (Table 1;entry 3) showing the intensity of CH_2 peaks of lactone at 1.64 ppm region.[5].

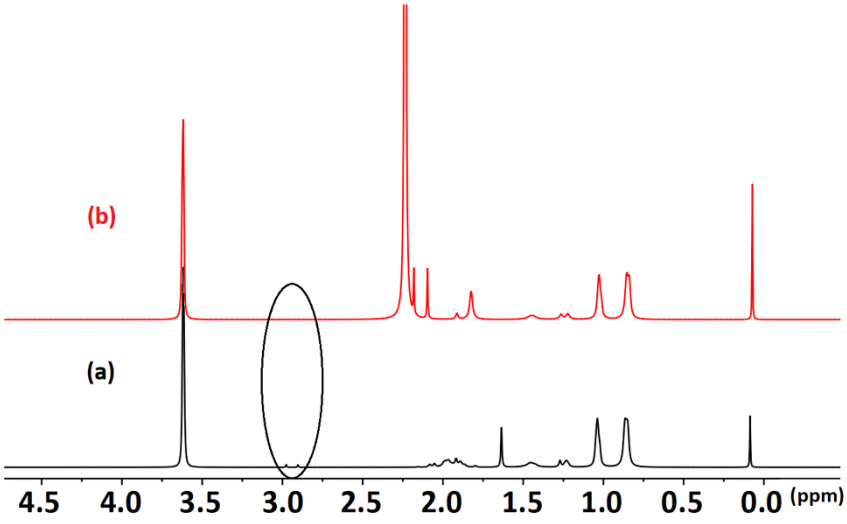

Figure S9. ^{1}H NMR spectra in both $CDCl_3$ of PMMA before (a) and after (b) adding acid anhydride.[6].

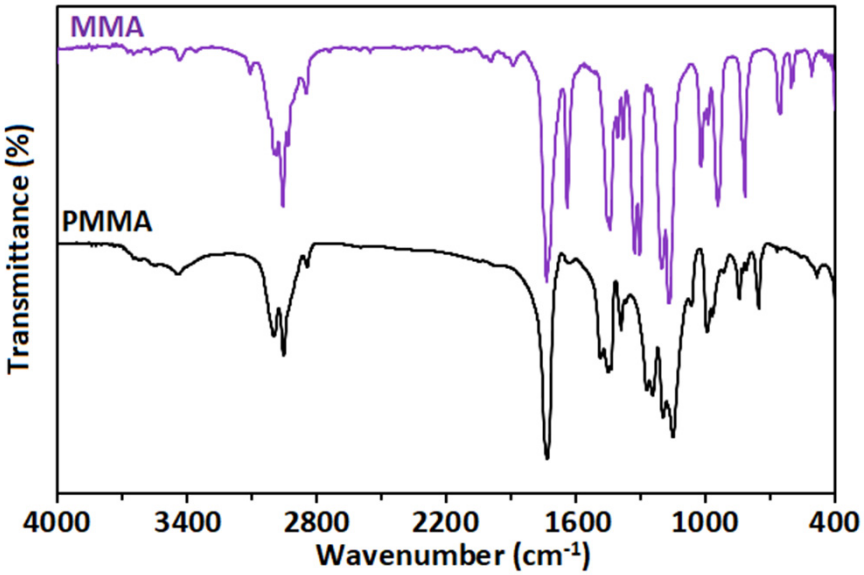

Figure S10. FT-IR spectra of monomer MMA and polymer PMMA obtained using ZIF-L as catalyst at 140 °C and [MMA]/[ZIF-L] = 50.

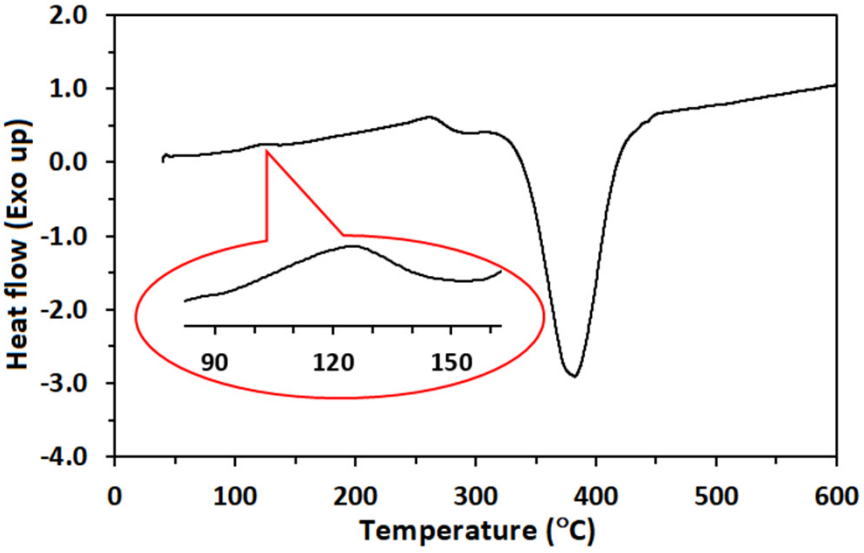

Figure S11. DSC thermogram of PMMA (Table 1, entry 3) determined under N_2 flow.

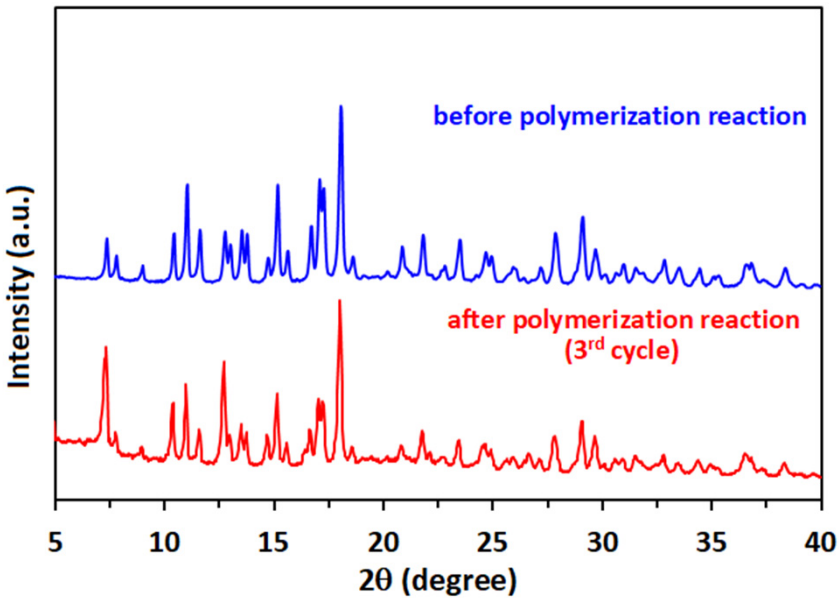

Figure S12. PXRD patterns of ZIF-L before and after the polymerization reaction. The compared results confirm the stability of the ZIF-L during polymerization.

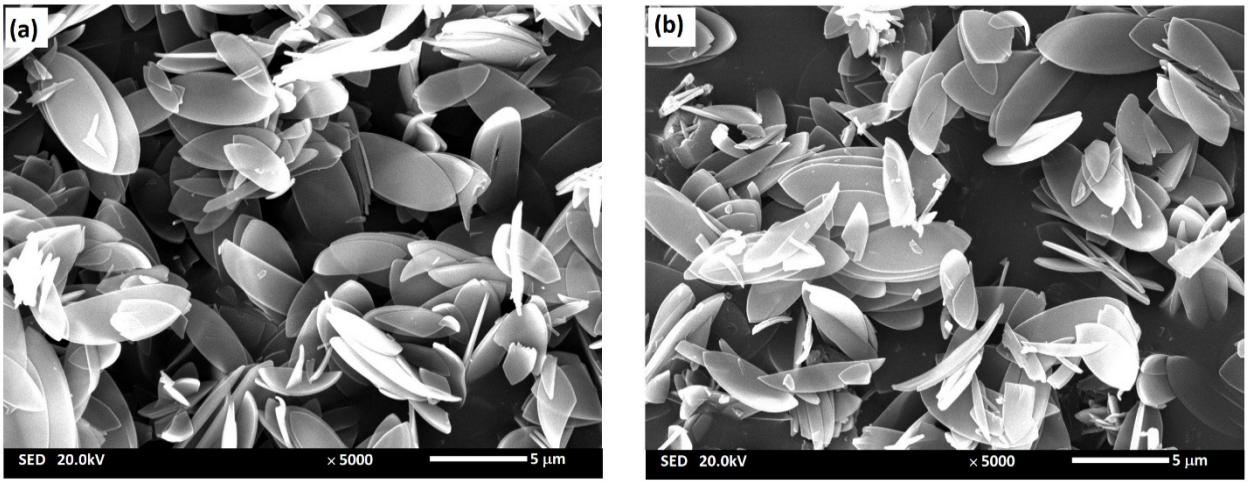

Figure S13. SEM micrographs of ZIF-L before (a) and after the polymerization reaction (b) (3rd cycle).

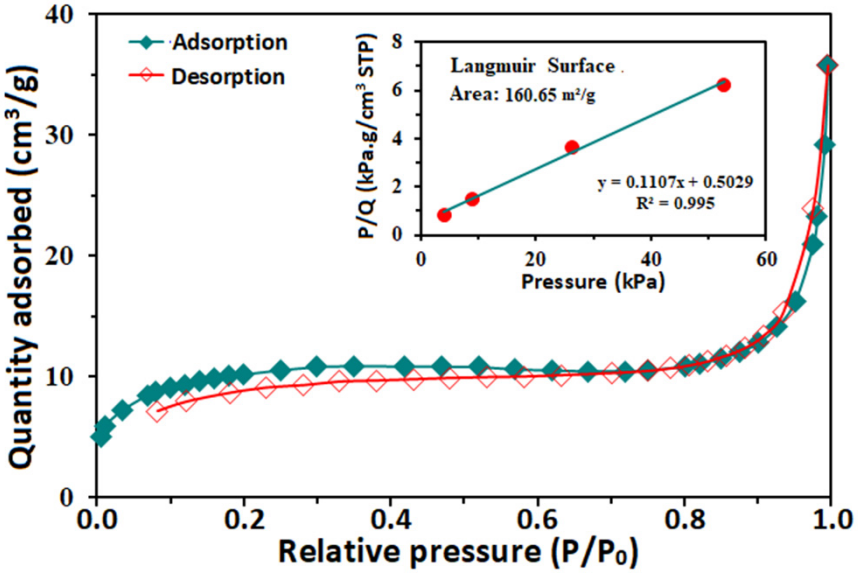

Figure S14. The nitrogen adsorption-desorption isotherms of the recovered ZIF-L after the polymerization (3rd cycle) measured at 77K.

Table S4. Elemental analysis (Zn metal) of the examined catalyst before and after the polymerization, mixture of solution, and synthesized PMMA using ICP method.

ICP analysis	Results
Pristine ZIF-L	29.33%
Recovered ZIF-L (after 3rd cycle)	28.85%
Filtrate after 1st cycle	120 μg L^{-1}
Filtrate after 3rd cycle	95 μg L^{-1}
PMMA [a]	0.0005%

[a]Reaction conditions: [MMA]/[ZIF-L] = 50; temperature = 140 °C; time = 24 h.

Table S5. Recycling studies of the examined catalyst (ZIF-L).

Run [a]	conv.[b] (%)	M_n [c] (kg/mol)	$Đ$ [c]	yield[d] (mg)
1	83	1390	1.12	193
2	80	1111	1.54	185
3	78	1095	1.62	179

[a]Reaction conditions: [MMA]/[ZIF-L] = [2.35 mM]/[0.047 mM] = 50; temperature = 140 °C; time = 24 h. [b]Calculated by ^{1}H-NMR in $CDCl_3$. [c]Determined by GPC analysis in THF at room temperature referenced to polystyrene standards, [d]Yield of PMMA observed experimentally.

References

1. Zhong, Z.; Yao, J.; Chen, R.; Low, Z.; He, M.; Liu, J.Z.; Wang, H. Oriented two-dimensional zeolitic imidazolate framework-l membranes and their gas permeation properties. *J. Mater. Chem. A* **2015**, *3*, 15715-15722.
2. Zhang, S.; Du, M.; Shao, P.; Wang, L.; Ye, J.; Chen, J.; Chen, J. Carbonic anhydrase enzyme-mofs composite with a superior catalytic performance to promote co2 absorption into tertiary amine solution. *Environ. Sci. Technol.* **2018**, *52*, 12708-12716.
3. Chen, R.; Yao, J.; Gu, Q.; Smeets, S.; Baerlocher, C.; Gu, H.; Zhu, D.; Morris, W.; Yaghi, O.M.; Wang, H. A two-dimensional zeolitic imidazolate framework with a cushion-shaped cavity for co2 adsorption. *Chem. Commun.* **2013**, *49*, 9500-9502.
4. Ding, B.; Wang, X.; Xu, Y.; Feng, S.; Ding, Y.; Pan, Y.; Xu, W.; Wang, H. Hydrothermal preparation of hierarchical zif-l nanostructures for enhanced CO_2 capture. *Colloid Interf. Sci.* **2018**, *519*, 38-43.
5. Wang, X.; Zhang, Y.; Hong, M. Controlled and efficient polymerization of conjugated polar alkenes by lewis pairs based on sterically hindered aryloxide-substituted alkylaluminum. *Molecules* **2018**, *23*, 442.
6. Peters, R.; Mengerink, Y.; Langereis, S.; Frederix, M.; Linssen, H.; van Hest, J.; van der Wal, S. Quantitation of functionality of poly(methyl methacrylate) by liquid chromatography under critical conditions followed by evaporative light-scattering detection: Comparison with nmr and titration. *J. Chromatogr. A* **2002**, *949*, 327-335.