

Electronic Supplementary Information

Free radical and RAFT polymerization of vinyl esters in metal-organic-frameworks

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Materials. Vinyl acetate (VAc, $\geq 99\%$, Sigma-Aldrich), vinyl propionate (VPr, 97%, Alfa Aesar), and vinyl butyrate (VBu, $> 98\%$, TCI) were distilled at reduced pressure from calcium hydride (95%, Sigma-Aldrich) prior to use. 2,2'-Azobis (isobutyronitrile) (AIBN, 98%, Sigma-Aldrich) was recrystallized from methanol (MeOH). Zn nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, Sigma-Aldrich), benzene-1,4-dicarboxylic acid (bdc, $> 99\%$, TCI), triethylenediamine (ted, 98%, Alfa Aesar), ethyl 2-bromopropionate (99%, Sigma-Aldrich), potassium *O*-ethyl xanthate (96%, Sigma-Aldrich), chloroform (CHCl_3 , analytical grade, Fisher Scientific), MeOH (analytical grade, Fisher Scientific), *n*-hexane (analytical grade, Fisher Scientific), dimethylformamide (DMF, analytical grade, VWR), and diethyl ether (ACS reagent, Sigma-Aldrich), were used as received.

Preparation of MOF. The host $[\text{Zn}_2(\text{bdc})_2(\text{ted})]_n$ was prepared by previously described method.¹ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 g, 3.36 mmol), bdc (0.560 g, 3.36 mmol), and ted (0.187 g, 0.168 mmol) were dissolved in DMF (40 mL). The mixture was heated in a Teflon-lined autoclave at 120 °C for 2 days. The crystalline precipitates were washed with DMF. The DMF was exchanged with volatile acetone to activate the MOF, followed by drying under a reduced pressure for 24 h at 85 °C.

Free Radical Polymerization in MOF. The host was dried under vacuum for 24 h at 85 °C prior to use. The feed solution ($[\text{AIBN}]: [\text{monomer}] = 1:471$) was incorporated into the dried host (250 mg) by wetness impregnation in a glove box. The excess monomer external to the host was removed by controlled evacuation at room temperature. Subsequently, the reaction tube was filled with nitrogen and immersed in thermostatic oil bath at 60 °C. After the polymerization, the host was etched by 0.05 M aqueous solution (15 mL) of sodium ethylenediaminetetraacetic acid (Na_2EDTA) to liberate the polymers. The solid components were collected by centrifugation and washed with distilled water for three times. The resulting solid was dissolved in CHCl_3 and filtered to remove insoluble product. The filtrate solution was concentrated and precipitated in a large amount of diethyl ether for PVAc, *n*-hexane for PVPr and MeOH for PVBu, repeatedly. The collected polymer was dried under vacuum at 50 °C overnight.

RAFT Polymerization in MOF. (*S*)-2-(ethyl propionate)-(*O*-ethyl xanthate) (X) was prepared according to the literature.² In a typical synthesis, 6.8 mL (9.48 g, 52.7 mmol) of ethyl-2-bromo-propionate was dissolved in 30 mL ethanol. 9.50 g (58 mmol) of potassium *O*-ethyl xanthate was added under stirring. After reaction for 16 h or more at room temperature, the white precipitates were filtered off. The filtrate was diluted with 250 mL diethyl ether and washed with 50 mL deionized water for four times, and dried over anhydrous magnesium sulfate. The yellowish liquid product was purified by column chromatography on silica gel

using hexanes/ethyl acetate (95: 5 v/v) as the eluent. A yellow colored oily product was obtained. $^1\text{H-NMR}$ (400 MHz, CDCl_3): 4.63 (q, 2H, C(O)OCH_2), 4.37 (q, 1H, CH), 4.20 (q, 2H, C(S)OCH_2), 1.56 (d, 3H, CH_3CH), 1.41 (t, 3H, $\text{C(O)-OCH}_2\text{CH}_3$), 1.28 (t, 3H, $\text{C(S)-OCH}_2\text{-CH}_3$).

The feed solution of [AIBN]: [X]: [monomer] = 1:3:471 was used. The other procedures are identical to those described in free radical polymerization in MOF.

Synthesis of Stereoregular Block Copolymer. Isotactic PVPr macro-RAFT agent prepared in MOF was used for chain extension with VAc at 60 °C ([AIBN]:[PVPr]:[VAc] = 0.4:1:2500). After three cycles of freeze-pump-thaw, the reaction tube was filled with nitrogen and immersed in thermostatic oil bath at 60 °C. After polymerization reaction for 1.5 h, the polymer was isolated in hexane, followed by drying under vacuum at 50 °C overnight.

Saponification of Poly(vinyl esters). For saponification of PVAc, a 15 % MeOH solution of KOH (1 mL) was added to a solution of PVAc (0.1 g) in MeOH (9 mL). The mixture was stirred for 2 h at 40 °C to yield poly(vinyl alcohol) (PVA) which is the MeOH-insoluble part. PVA was collected by centrifugation and washed with MeOH containing a small amount of acetic acid for three times. PVA was dried under vacuum for 12 h at 60 °C. For saponification of PVPr and PVBu, the polymers were dissolved in THF (9 mL) instead of MeOH. The other procedures are identical to those described for PVAc.

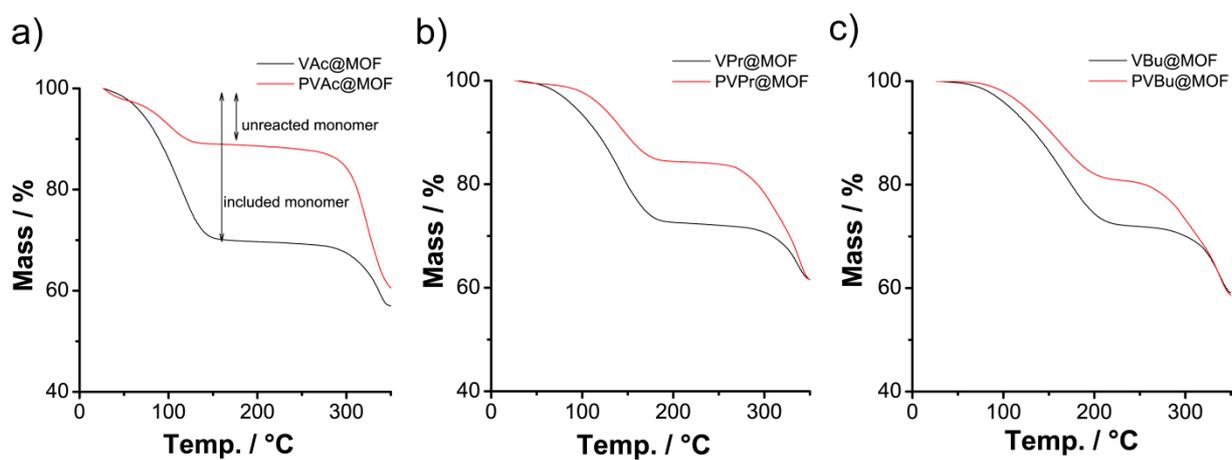
Characterization. The crystal structure of host was confirmed by powder X-ray diffractometer (PXRD) using Cu-K α radiation ($\lambda = 0.154$ nm) and a scintillation counter (KeveX Detector). Nitrogen adsorption and desorption experiments were performed using Quantachrome Quadrasorb at 77 K. Thermogravimetric analysis (TGA) was performed to determine monomer conversion for polymerizations in MOF. ^1H nuclear magnetic resonance (NMR) spectroscopies were recorded on an Ascend 400 Hz NMR spectrometer (Bruker) in

CDCl_3 for poly(vinyl ester)s and in $\text{DMSO-}d$ for PVA at ambient temperature. Size exclusion chromatography (SEC) was conducted in THF with toluene as internal standard at 25 °C using a column system by PSS SDV 1000/100000/1000000 column (8 x 300 mm, 5 μm particle size) with a PSS SDV precolumn (8 x 50 mm), a SECcurity RI detector and a SECcurity UV/VIS detector and a calibration with PS standards from PSS. The polydispersity was defined as $D = M_w/M_n$. The theoretical number average molecular mass $M_{n,\text{theo}}$ in chain extension was calculated according to the equation: $([\text{monomer}]_0/[\text{RAFT agent}]_0) \times \text{MW}_{\text{monomer}} \times \text{conversion} + \text{MW}_{\text{RAFT agent}}$. The monomer conversion in chain extension was determined by $^1\text{H NMR}$ in CDCl_3 at ambient temperature.

Table S1. Free Radical^a and RAFT Polymerization^b of Vinyl Ester in bulk.

Sample	Conv. [%] ^c	$M_{n, SEC}$ [g mol ⁻¹] ^d	\bar{D}	Tacticity ^e [%] mm:mr:rr (m)
<i>f</i> -PVAc in bulk	72	150000	3.79	22: 50: 28 (47)
<i>f</i> -PVPr in bulk	96	82100	4.14	22: 49: 29 (47)
<i>f</i> -PVBu in bulk	96	128000	3.36	20: 50: 30 (45)
<i>r</i> -PVAc in bulk	90	20900	1.21	22: 50: 28 (47)
<i>r</i> -PVPr in bulk	95	18300	1.56	22: 50: 28 (47)

^a [AIBN]: [monomer]=1:471 at 60 °C for 1 h. ^b [AIBN]: [RAFT agent]: [monomer]=1:3:471 at 60 °C for 3 h. ^c Determined gravimetrically. ^d Determined by SEC against PS calibration. ^e Determined by ¹H NMR in DMSO-*d*₆ at ambient temperature.

**Figure S1.** TGA profiles for (vinyl ester)@MOF composites before and after polymerization.

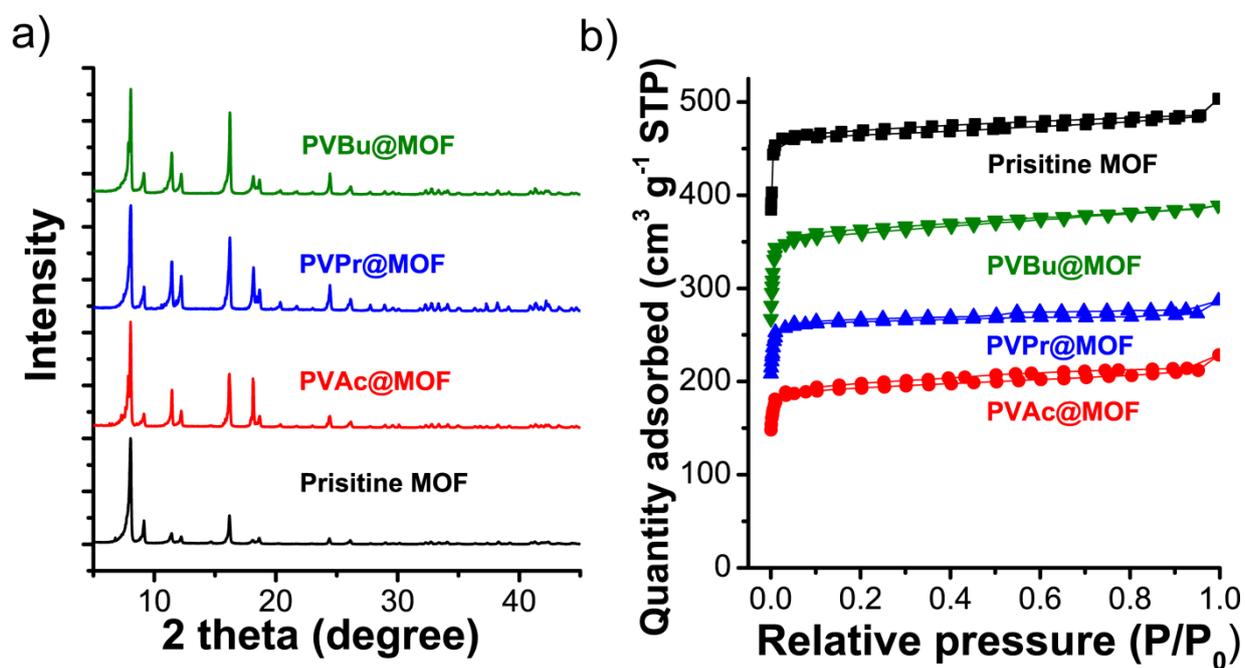


Figure S2. (a) PXRD patterns and (b) N₂ gas physisorption isotherms of MOF and polymer@MOF composites after polymerization.

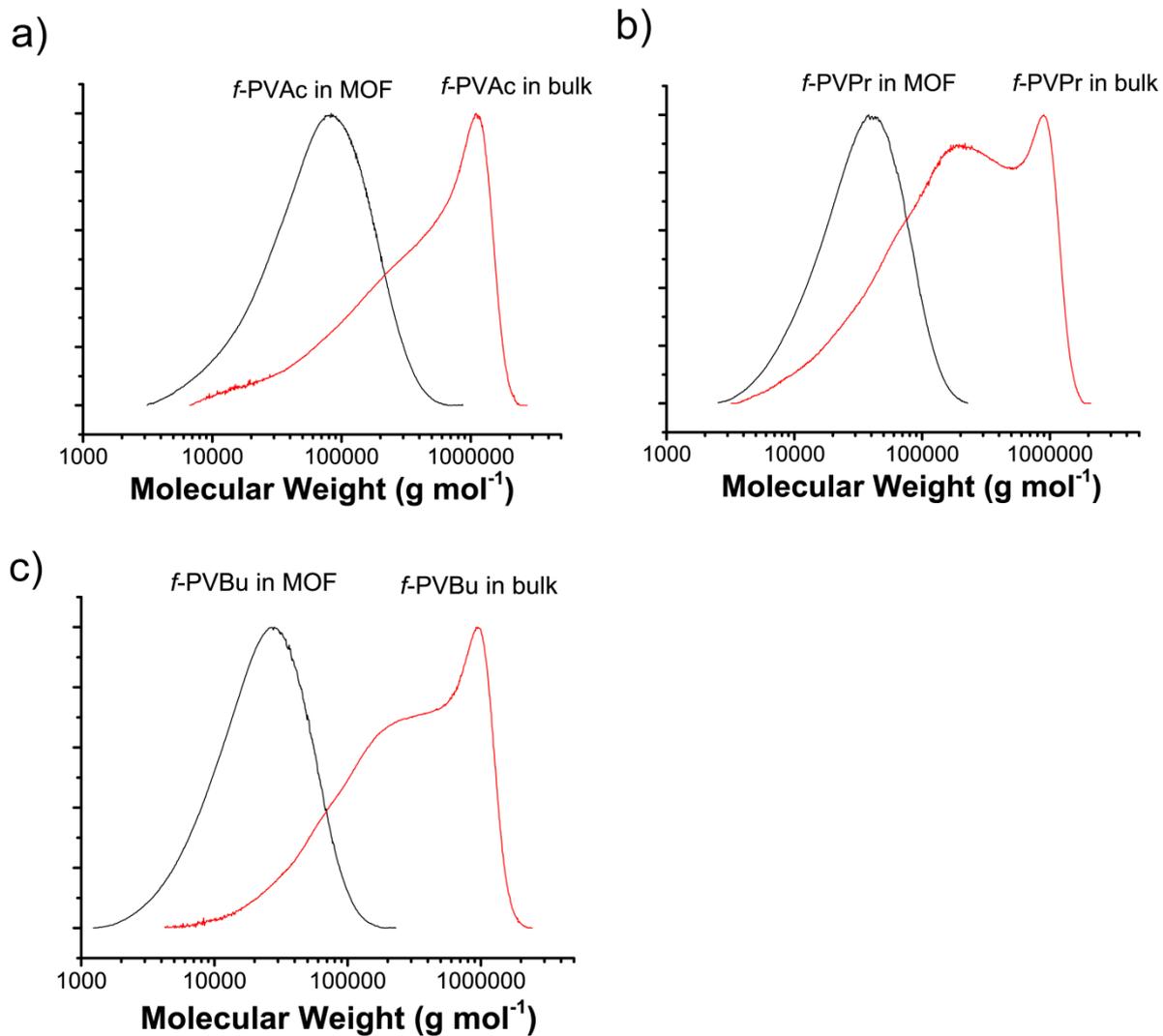


Figure S3. MWDs (obtained *via* SEC in THF with PS calibration) of (a) *f*-PVAc (b) *f*-PVPr and (c) *f*-PVBu prepared in MOF and in bulk.

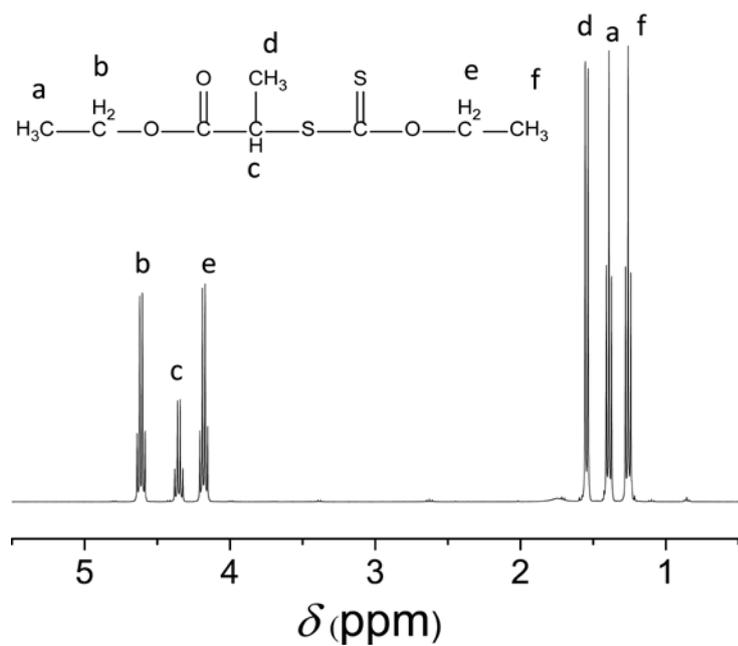


Figure S4. $^1\text{H-NMR}$ of *(S)*-2-(ethyl propionate)-(O-ethyl xanthate) recorded in CDCl_3 at ambient temperature.

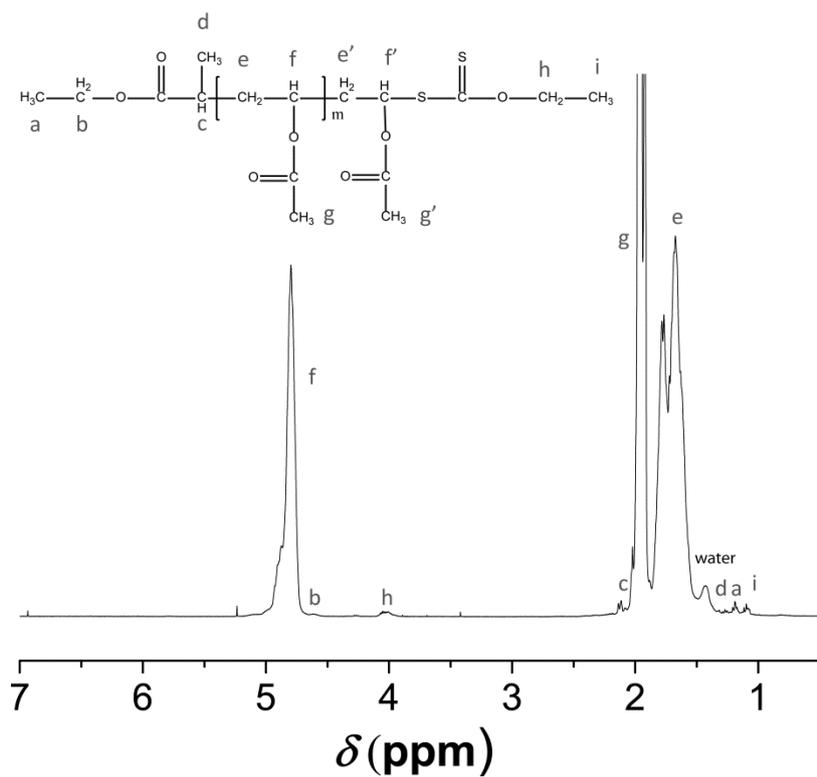


Figure S5. $^1\text{H-NMR}$ of *r*-PVAc polymerized in MOF recorded in CDCl_3 at ambient temperature.

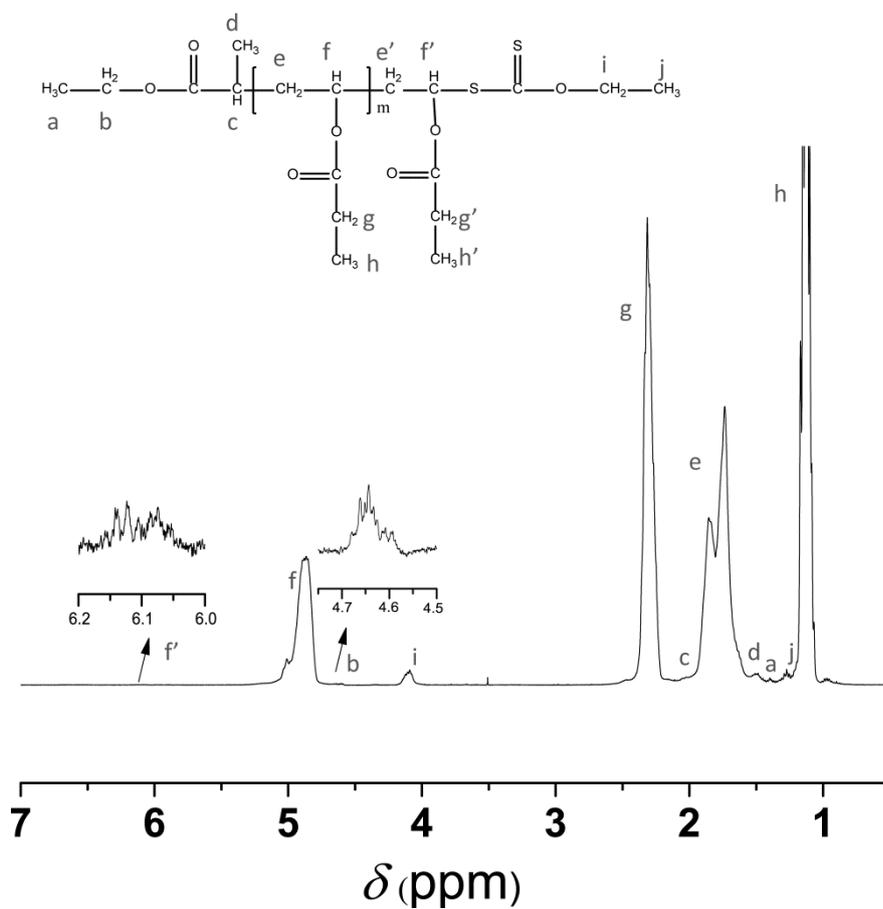
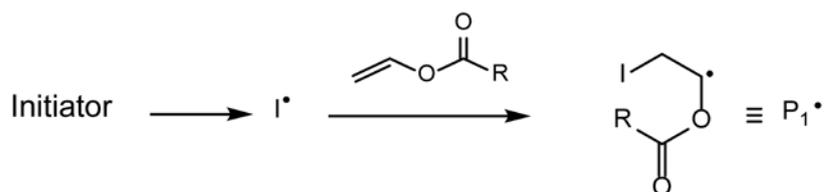
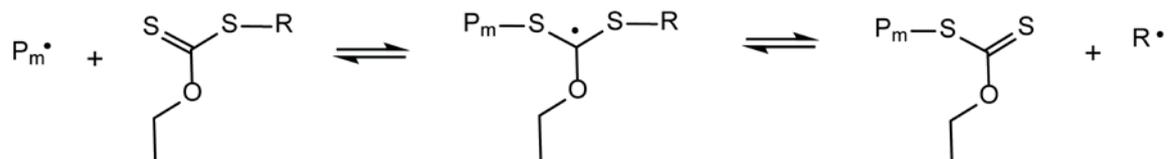


Figure S6. ¹H-NMR of *r*-PVPr polymerized in MOF recorded in CDCl₃ at ambient temperature.

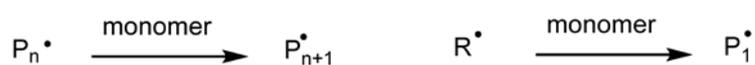
i) Initiation



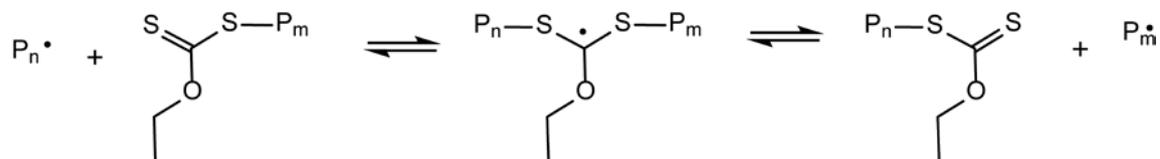
ii) Pre-equilibrium



iii) Propagation



iv) Degenerate Transfer: Core (main) equilibrium



v) Termination



Figure S7. Xanthate mediated RAFT process of vinyl ester.

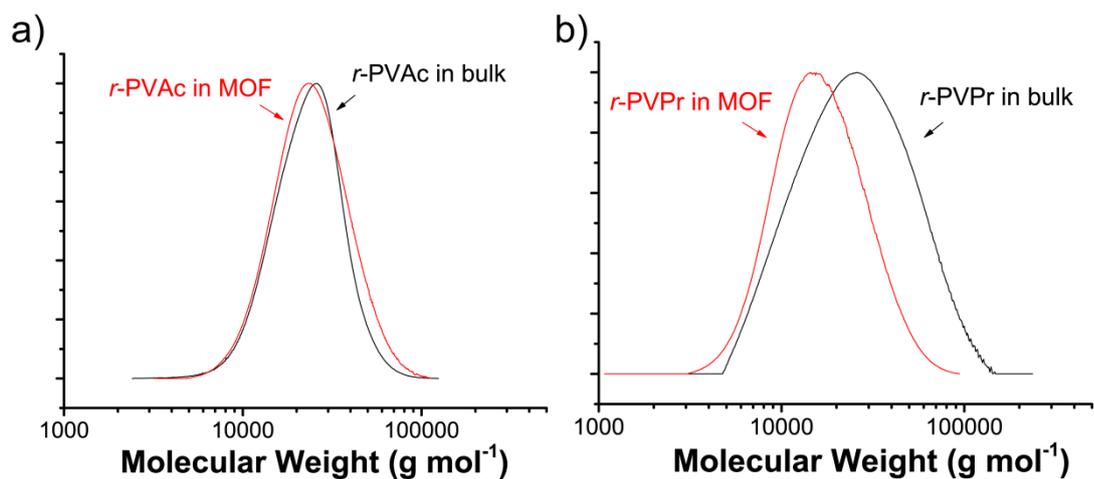


Figure S8. MWDs (obtained *via* SEC in THF with PS calibration) of (a) *r*-PVAc and (b) *r*-PVPr prepared in MOF and in bulk.

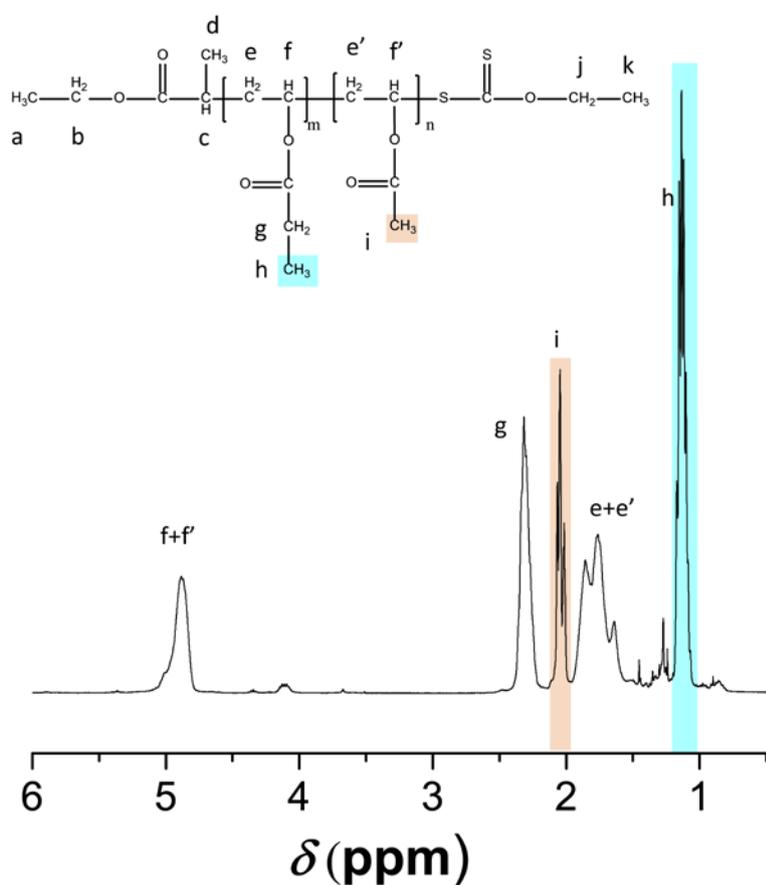


Figure S9. ^1H NMR of *it*PVPr-*b-at*PVAc block copolymer recorded in CDCl_3 at ambient temperature.

Reference

- 1) Dybtsev, D. N.; Chun, H.; Kim, K. Rigid and Flexible: A Highly Porous Metal–Organic Framework with Unusual Guest-Dependent Dynamic Behavior. *Angew. Chem., Int. Ed.* **2004**, *43*, 5033-5036.
- 2) Patel, V. K.; Vishwakarma, N. K.; Mishra, A. K.; Biswas, C. S.; Ray, B. (*S*)-2-(Ethyl Propionate)-(*O*-Ethyl Xanthate)-and (*S*)-2-(Ethyl Isobutyrate)-(*O*-Ethyl Xanthate)-Mediated RAFT Polymerization of Vinyl Acetate. *J. Appl. Polym. Sci.* **2012**, *125*, 2946-2955.