

Electronic Supplementary Information

**Radical Polymerization of 2,3-Dimethyl-1,3-butadiene in
Coordination Nanochannels**

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Experimental details

Materials. All of the reagents and chemicals used were obtained from commercial sources, unless otherwise noted. PCP hosts were prepared using previously described methods.^{1,2} DMB was purified by vacuum distillation prior to use. 2,2'-Azobis(isobutyronitrile) was recrystallized from MeOH solution.

Polymerization of DMB in PCPs. A typical procedure for polymerization of DMB in PCPs is as follows. After drying a host PCP (200 mg) by evacuation (<0.1 kPa) at 135 °C for 8 h in a Pyrex reaction tube, the PCP powder was immersed in DMB (1 mL) with AIBN (4 mg) at room temperature for 0.5 h to introduce the monomer and initiator into the nanochannels. After excess monomer external to the host crystals was removed completely by evacuation (10 kPa) at room temperature for 0.5 h, the reaction tube was filled with nitrogen, and heated to 60 °C to perform the polymerization over a period of 48 h. The obtained composite was washed with MeOH, and vigorously stirred for two days in a mixture of hexane (100 mL) and 0.05 M aqueous solution (100 mL) of sodium ethylenediaminetetraacetate (Na-EDTA), resulting in a clear bilayer solution without residual PCPs and precipitates. Then, the organic layer was separated and evaporated to give PDMB.

Measurements. The X-ray powder diffraction (XRPD) data were collected using a Rigaku RINT 2000 Ultima diffractometer employing CuK α radiation. The ¹H spectra were obtained using a JEOL ECA-600P spectrometer operating at 600 MHz. The thermogravimetric (TG) analysis was carried out from room temperature to 500 °C at a heating rate of 10 °C min⁻¹ using a Rigaku Instrument Thermo Plus TG 8120 in a nitrogen atmosphere. The amount of DMB adsorbed in PCPs was determined from the weight loss up to 200 °C by TGA. Differential scanning calorimetry (DSC) was carried out at a heating rate of 10 °C min⁻¹ with Seiko Instruments DSC 6220 under N₂ atmosphere. Gel permeation chromatography (GPC) measurements on the resulting polymers were performed in CHCl₃ at 40 °C on three linear-type polystyrene gel columns (Shodex K-805L) that were connected to a JASCO PU-980 precision pump, a JASCO RI-930 refractive index detector, and a JASCO UV-970 UV/vis detector set at 256 nm. The columns were calibrated against standard polystyrene samples. Electron spin resonance (ESR) measurements were conducted using a Bruker EMX spectrometer. Radical concentration was determined by using CuSO₄ crystals as an external standard.

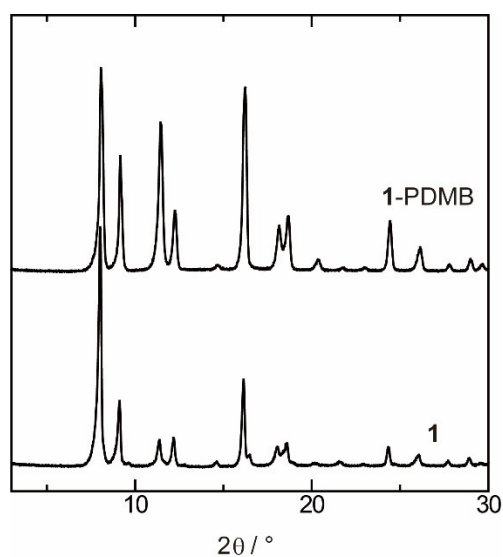


Figure S1. XRD patterns of **1** and **1**-PDMB composite.

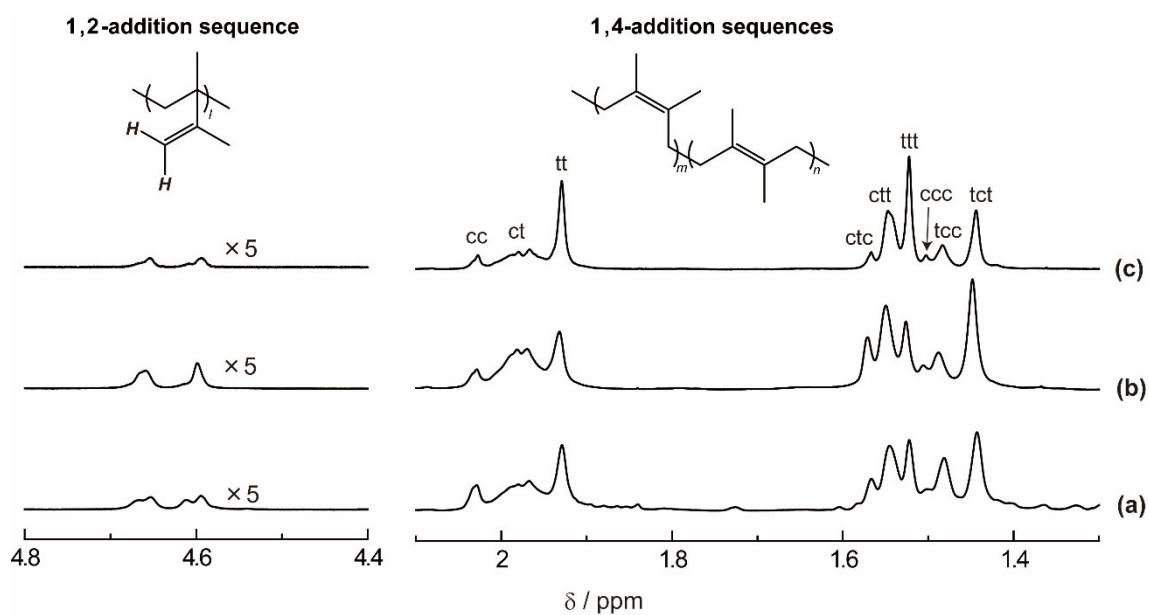


Figure S2. ^1H NMR spectra of PDMB obtained from (a) bulk condition, (b) **1**, and (c) $[\text{Cu}_2(2,5\text{-dimethoxyterephthalate})_2(\text{ted})]_n$ in benzene- d_6 . Overall contents of *cis* and *trans* units can be determined from the spectra for 1,4-addition sequences, where diads and triads of these structural units are clearly observed (c and t denote *cis* and *trans* configurations, respectively).

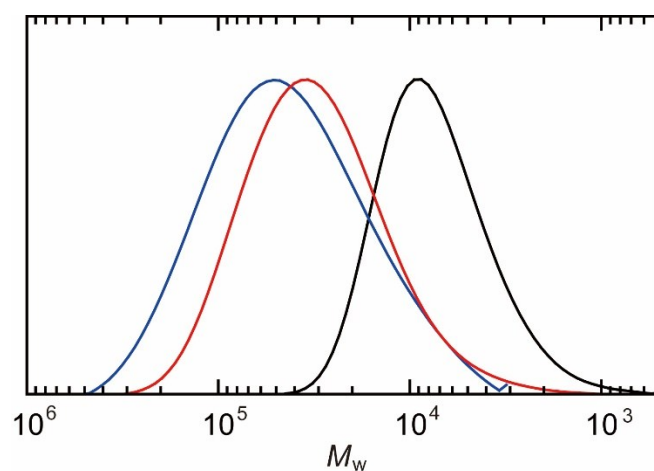


Figure S3. GPC profiles of PDMB prepared in bulk (black) and the nanochannels of **1** (red) and $[\text{Cu}_2(\text{bdc})_2(\text{ted})]_n$ (blue).

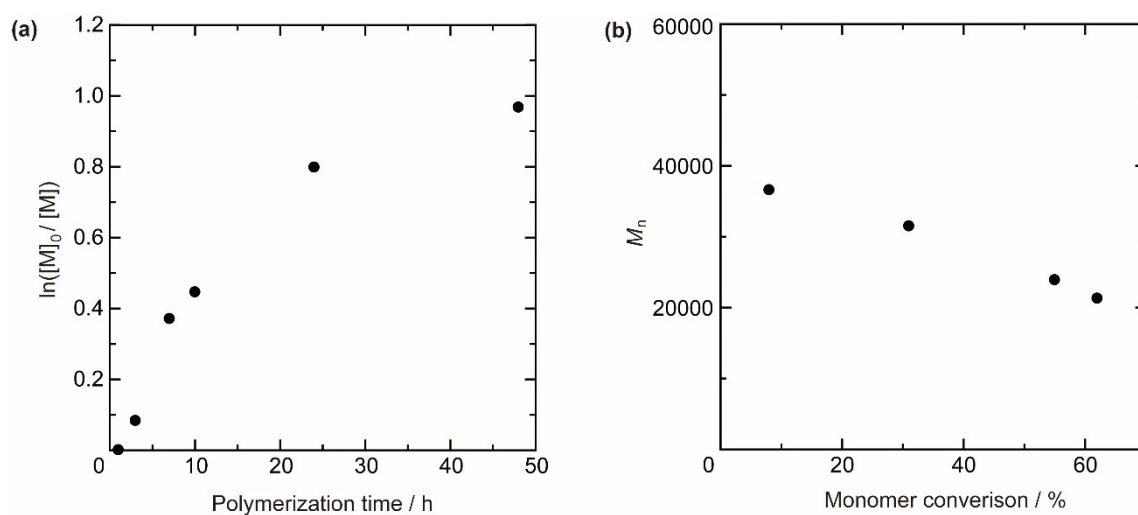


Figure S4. (a) Kinetic plot and (b) dependence of M_n on monomer conversion for the polymerization of DMB in **1**.

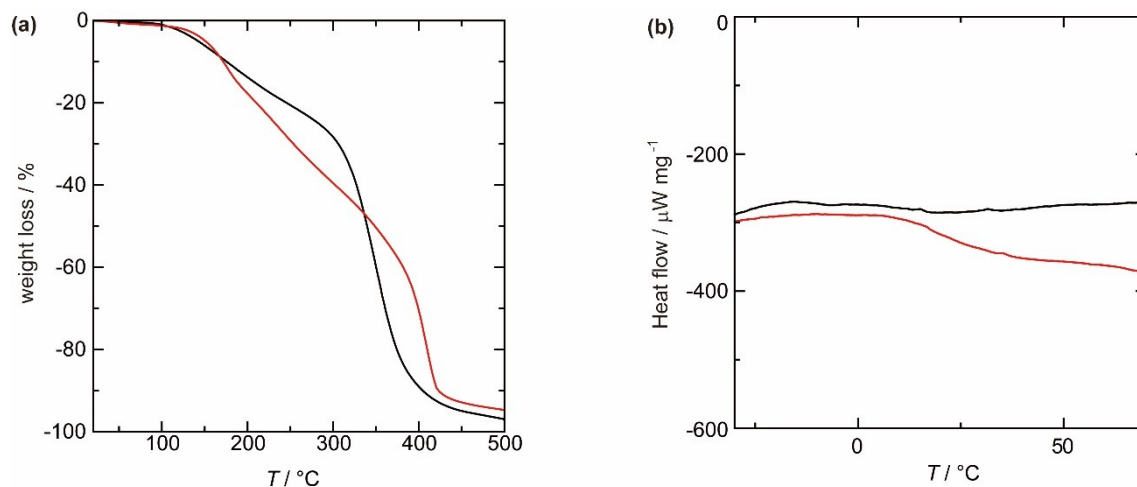


Figure S5. (a) TG and (b) DSC curves of PDMB obtained from bulk radical polymerization (black) and $[\text{Cu}_2(2,5\text{-dimethoxyterephthalate})_2(\text{ted})]_n$ (red). The TG curves of these two polymers did not overlap completely, showing different thermal degradation process. A previous paper reported that glass transition temperature (T_g) of highly *cis*- and *trans*-PDMB appeared at 2 and 22 °C, respectively, whereas PDMB prepared in free radical condition did not show a well-defined endotherm.³ This was ensured by our DSC measurements where no endothermic peak was observable for the bulk-synthesized PDMB. In contrast, the PDMB obtained from the PCP presented a clear endothermic peak at 13 °C, probably because of the regulated structure with high 1,4-*trans* content.

References

- 1) T. Umeura, Y. Ono, K. Kitagawa, and S. Kitagawa, *Macromolecules* 2008, **41**, 87.
- 2) T. Uemura, Y. Ono, Y. Hijikata, and S. Kitagawa, *J. Am. Chem. Soc.* 2010, **132**, 4917.
- 3) B. Gordon III and M. Blumenthal, *Polym. Bull.* 1985, **14**, 69.