Electronic Supplementary Information (ESI) for denitrogen alkene polymerization of bisdiazo compounds by copper(II) catalysts

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Experimental details

Materials.

Bisdiazo compounds were synthesized according to literature.[1] The copper catalysts were purchased from Alading and used as received. All the solvents were dried by CaH_2 for 24 h and distilled before they were used.

General Instrumentations.

^{1}H NMR spectrum was recorded on a Mecury VX-300 spectrometer (300 MHz) using d_6-DMSO as solvent. Molecular weight (M_n) and polydispersity (M_w/M_n, PDI) of the obtained polymers were determined by gel permeation chromatography (GPC) using polystyrene as standards with THF as eluent (1.0 mL min^{-1}). The GPC system was equipped with a Waters 717 plus auto sampler, a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, and Shodex K-805, K-804, and K-802.5 columns in series. The temperatures of the columns and detector were both 30 ^{o}C. Differential scanning calorimeter (DSC) was performed on a Q20 (TA) instrument with nitrogen as the protecting gas. The samples were heated from -30 to 100 ^{o}C, hold for 10 min to erase the thermal history, then cooled to -30 ^{o}C at a rate of 10 ^{o}C min^{-1}, and finally heated to 100 ^{o}C at a rate of 10 ^{o}C min^{-1}. X-Ray diffraction (XRD) was recorded on a Bruker D8-advance with the scan speed of 6^{o} min^{-1}. Flourier transformed infrared spectroscopy (FT-IR) spectrum were recorded on Thermo iS10 spectrometer. Scanning electron microscopy (SEM) measurements of the obtained polymers were performed on a Sirion 200 field emission scanning electron microscope (FEI Co., Eindhoven) at an accelerating voltage of 12 kV. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectrum was collected with an Axima TOF2 mass spectrometry (Shimadzu). The instrument was equipped with a 3 ns pulse width 337 nm nitrogen laser. All of the mass spectra were obtained in positive ion mode at an accelerating voltage of 20 kV and 200 laser shots were averaged to generate each spectrum.

Experiment section.

Typical procedure for polymerization: Cupric(II) acetylacetonate 2a (1×10^{-5} mol) was dissolved in 50 mL toluene under stirring in a three-necked bottle, and then refluxed at 100^{o}C. Bisdiazo compound 1a (1×10^{-3} mol) was dissolved in 50 mL toluene and added dropwise to the above catalyst system. After 24 h, the reaction mixture were cooled to room temperature and then concentrated under reduced pressure. The product was then dissolved in toluene, precipitated in methanol, and filtered. The powder product was collected and dried under vacuum.

Reference.

1. G. Y. Li and C. M. Che, *Organic Letters*, 2004, **6**, 1621-1623.

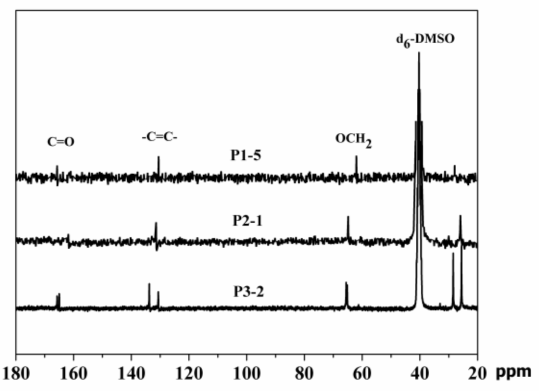

Figure S1. ^{13}C NMR spectra of polymers obtained by DNAP.

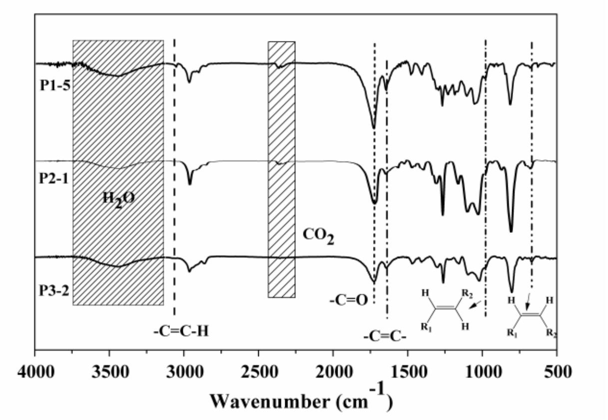

Figure S2. FTIR spectra of polymers obtained by DNAP.

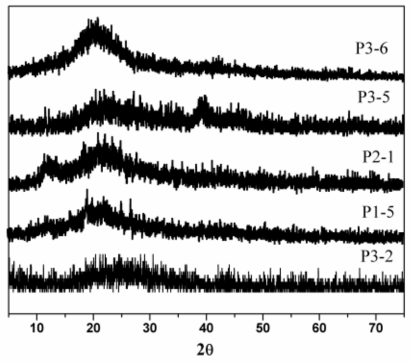

Figure S3. XRD spectra of polymers obtained by DNAP.

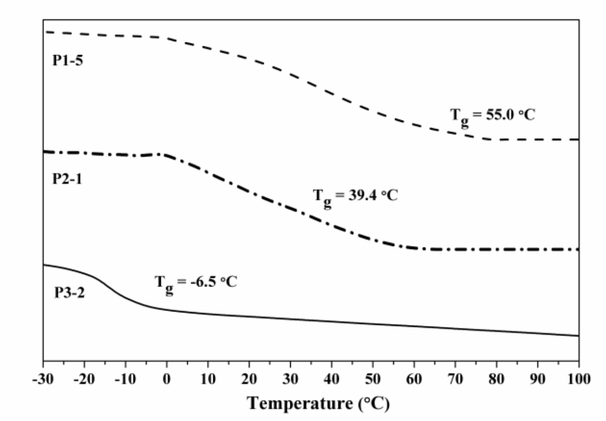

Figure S4. DSC spectra of polymers obtained by DNAP.