

Supporting Information for
Intra- and Intermolecular Hydrogen Bonding in Miscible Blends of
CO₂/Epoxy Cyclohexene Copolymer with Poly(vinyl phenol)

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Ligand LH

A solution of 2,2-dimethyl-1,3-propanediamine in moderate MeOH was added dropwise to 2 equiv. of *o*-vanillin solution. The mixture was stirred for 4 h at room temperature and then the solvent was evaporated under vacuum to obtain a yellow powder. This synthesis was performed based on the report from the Williams group.¹ ¹H NMR (500 MHz, CDCl₃, δ, ppm): 1.07 (s, 6H, CCH₃), 3.49 (s, 4H, NCH₂), 3.91 (s, 6H, OCH₃), 6.77–6.95 (m, 6H, ArH), 8.32 (s, 2H, N=CH), 14.15 (br, 2H, COH). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 24.3 (CCH₃), 36.3 (C-CH₃), 56.2 (OCH₃), 67.5 (NCH₂), 114.3–123.5 (ArC), 149.1 (COCH₃), 152.8 (COH), 166.6 (N=C). FTIR (KBr, cm⁻¹): 1632 (aromatic C=C), 3450 (O-H).

Catalyst LZn₂(OAc)₂

A solution of Zn(OAc)₂·2(H₂O) (2 equiv.) in MeOH was added to a solution of LH and then the mixture was stirred at room temperature overnight. Evaporation of the solvent vacuo provided a yellow powder. Washing with hexane, followed by crystallization from THF/hexane, yielded LZn₂(OAc)₂. This synthesis was performed based on a report from the Williams group.¹ ¹H NMR (500 MHz, CDCl₃, δ, ppm): 1.03 (s, 6H, CCH₃), 1.97 [s, C(O)CH₃, 6H], 3.74 (s, 4H, NCH₂), 3.86 (s, 6H, OCH₃), 6.50–6.90 (m, 6H, ArH), 8.04 (s, 2H, N=CH). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 23.3 [C(O)CH₃], 25.4 (C-CH₃), 35.5 (CCH₃), 56.0 (OCH₃), 75.0 (NCH₂), 114.2–118.6 (ArC), 127 (COCH₃), 150.9 (C-OH), 171.1 (N=C). FTIR (KBr, cm⁻¹): 1624 (aromatic C=C).

Characterization

¹H and ¹³C NMR spectra were recorded using an INOVA 500 MHz NMR spectrometer, with CDCl₃ as an external standard. Weight average (*M_w*) and number average (*M_n*) molecular weights and polydispersity indexes (*M_w*/*M_n*) were determined using a Water 510 gel permeation chromatograph. IR spectra were recorded using a Bruker Tensor 27 FTIR spectrophotometer and the conventional

crystal KBr disk method; 32 scans were collected at a spectral resolution of 4 cm^{-1} ; a temperature-controlled compartment holder was used to record FTIR spectra at various temperatures, to maintain dry sample films. Glass transition temperatures were measured using a TA Q-20 differential scanning calorimeter; approximately 5 mg of sample was placed on a DSC sample pan and heated from 40 to $180\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under a N_2 atmosphere (50 mL min^{-1}). High-resolution solid state ^{13}C NMR spectroscopy was performed at $25\text{ }^{\circ}\text{C}$ using a Bruker AVANCE III spectrometer operated at a resonance frequency of 100.62 MHz . The experiments were performed using the cross-polarization (CP)/magic-angle spinning (MAS)/high-power dipolar decoupling (DD) technique. The proton spin-lattice relaxation time in the rotating frame ($T_{1\rho}\text{H}$) was determined through carbon observation using a 90° τ -spin lock pulse sequence prior to CP. The acquisition was performed at delay times (s) ranging from 0.1 to 30 ms with a contact time of 1.0 ms.

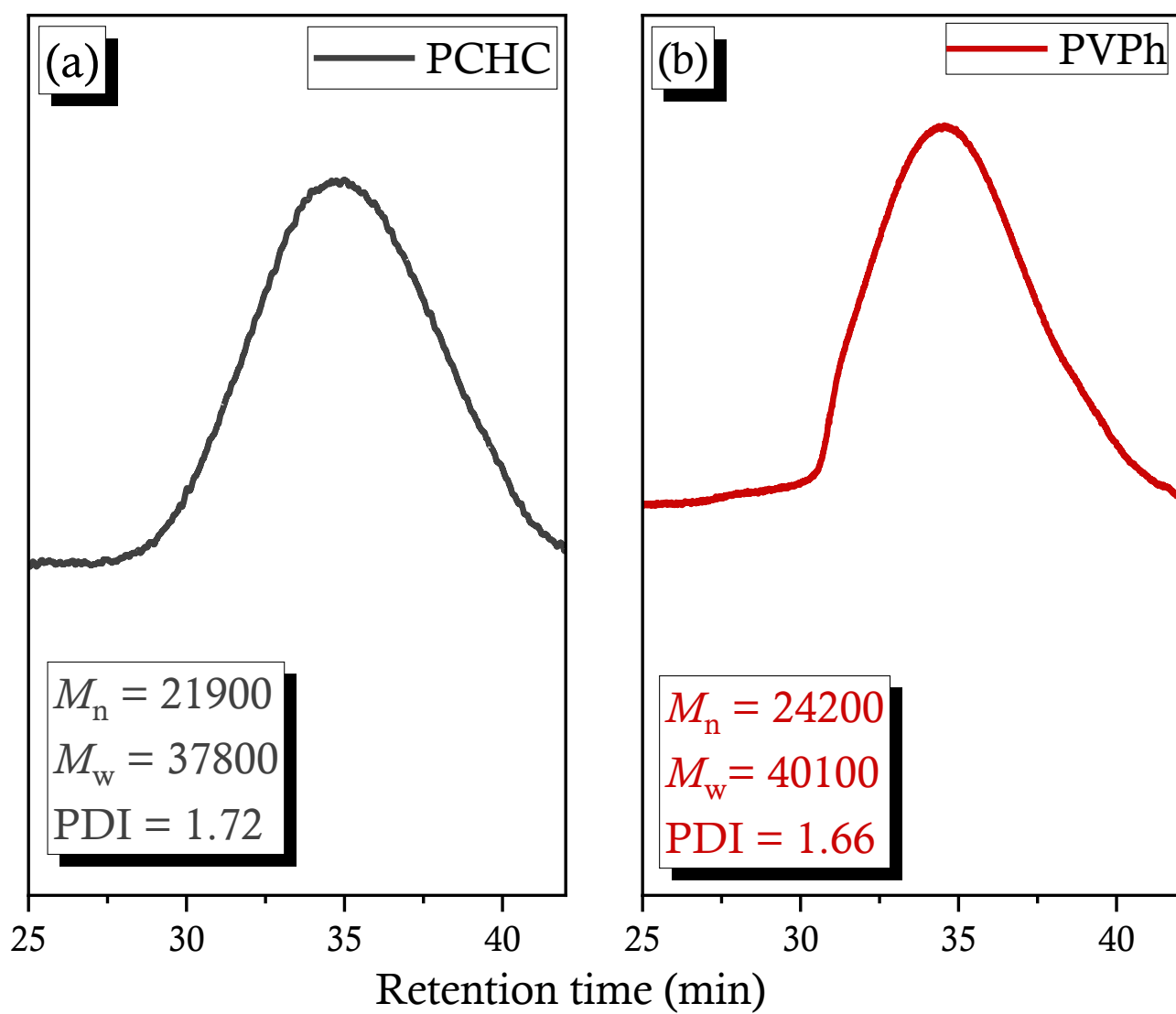


Figure S1: GPC analyses of (a) pure PCHC copolymer and (b) PVPh homopolymer

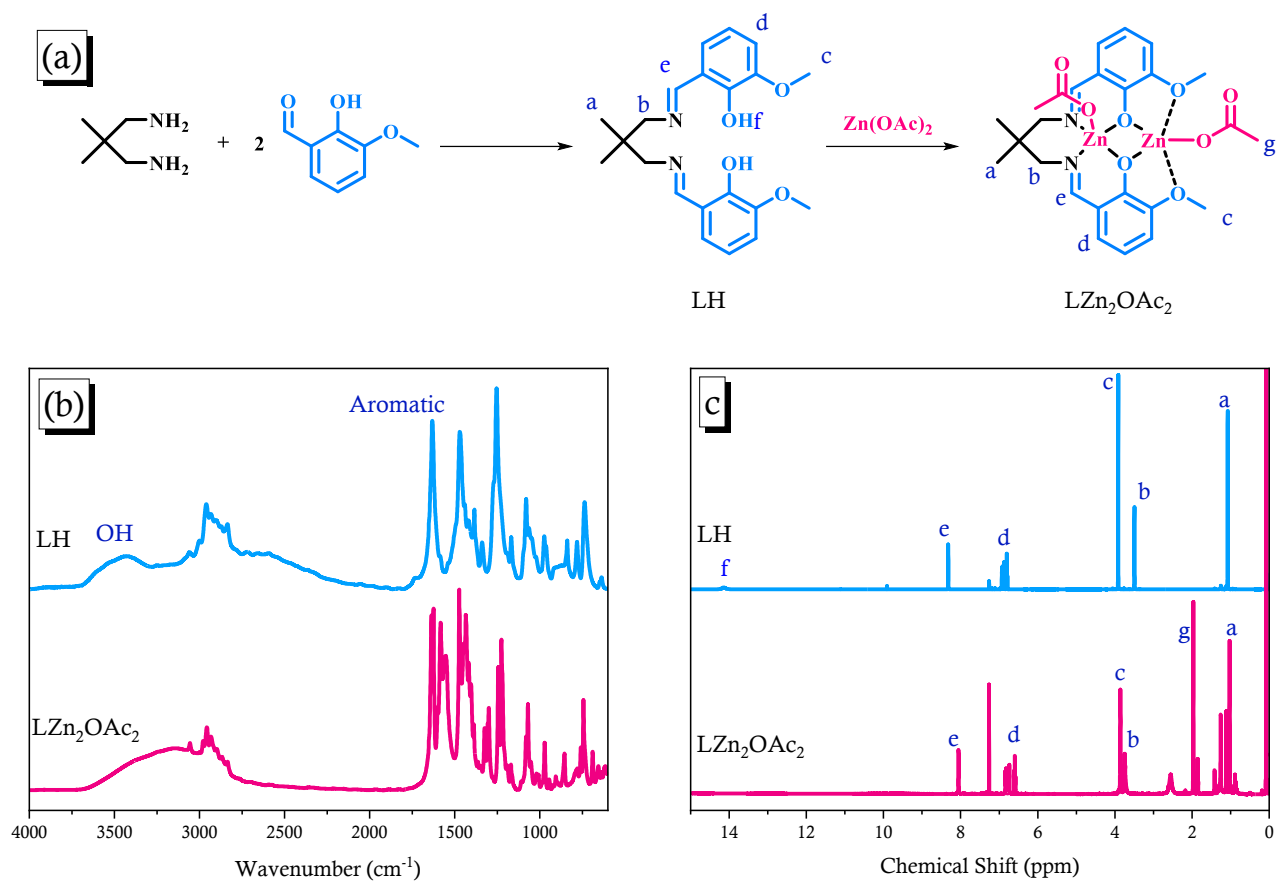


Figure S2: (a) The synthesis of LH and LZn₂OAc₂, (b) its related corresponding FTIR spectra and (c) ¹H NMR spectra

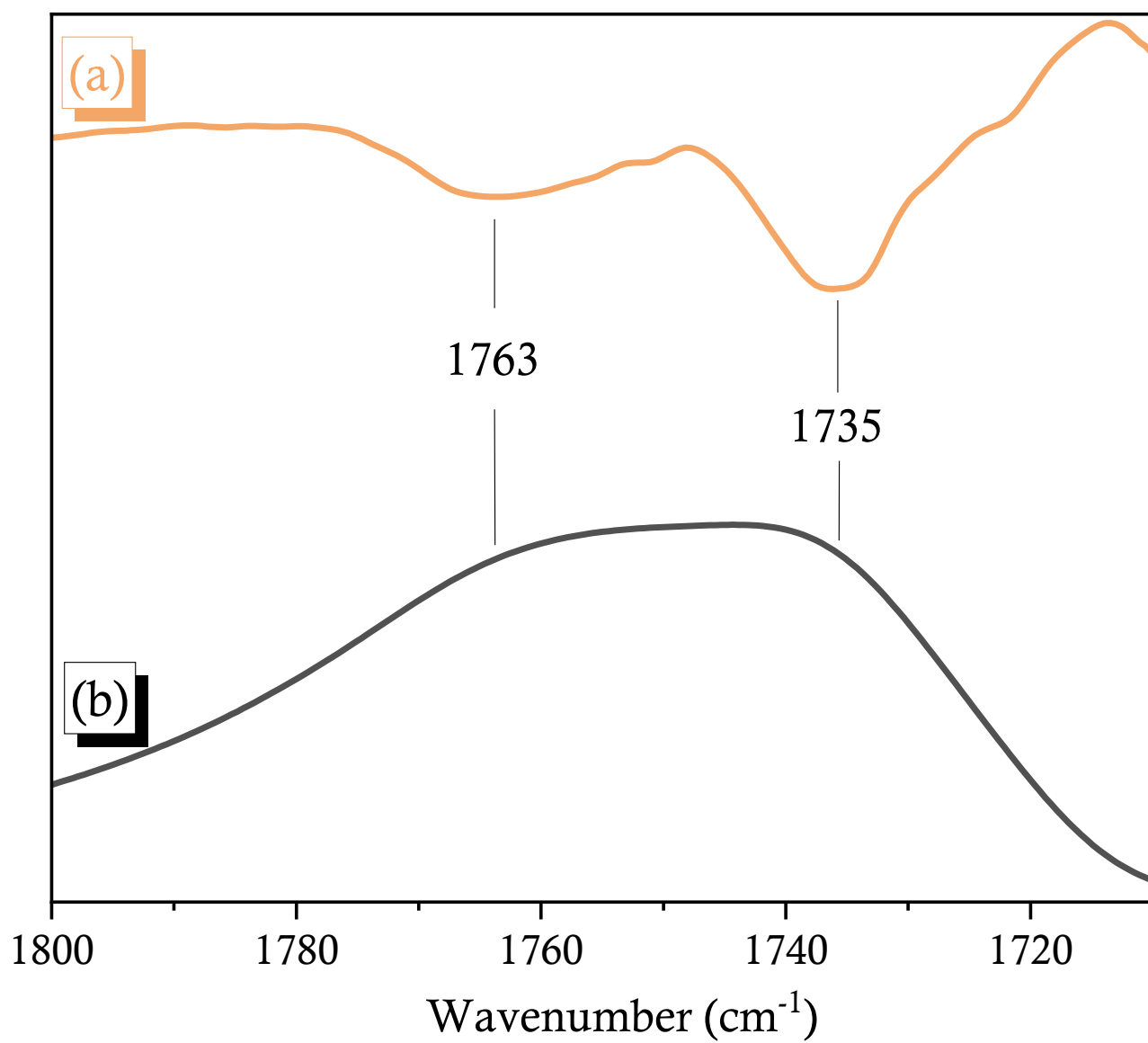


Figure S3: FTIR spectrum of C=O absorption and its second derivative spectrum of PCHC copolymer at 120 °C

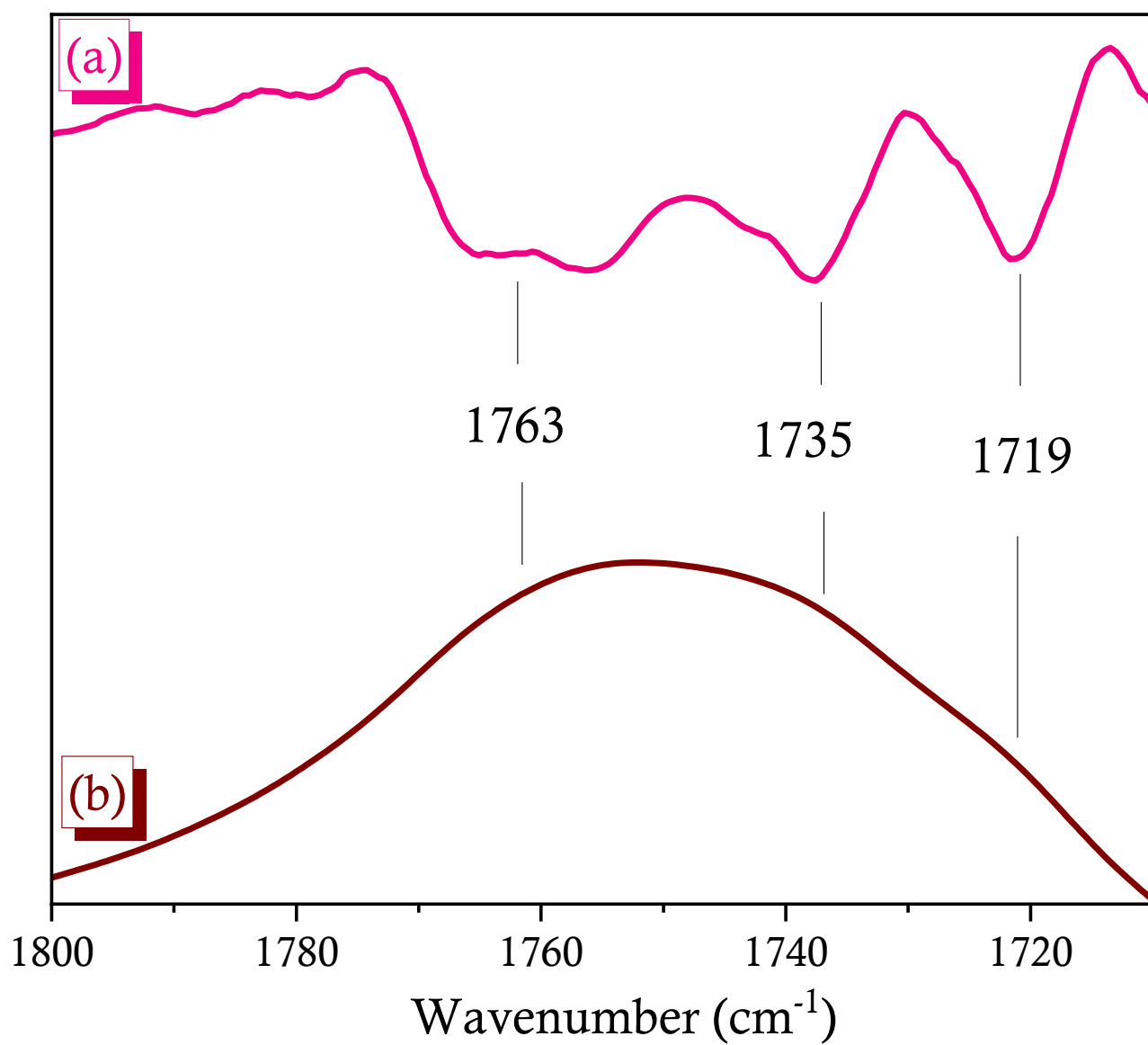


Figure S4: The IR spectrum of C=O absorption and its second derivative spectrum of PCHC-50 blend at 120 °C

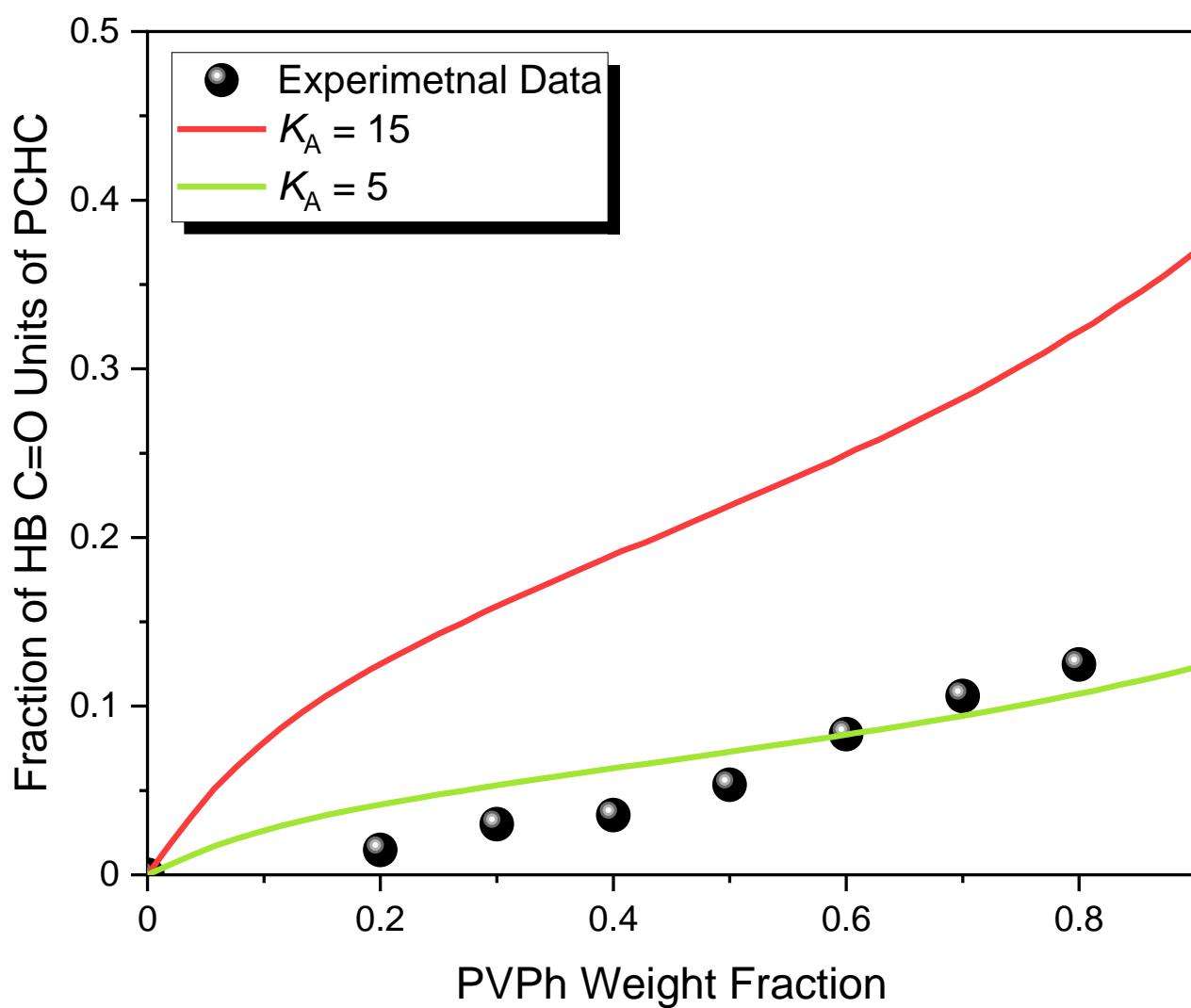


Figure S5: Experimental data about fraction of H-bonded C=O units of PCHC and predicted by PCAM

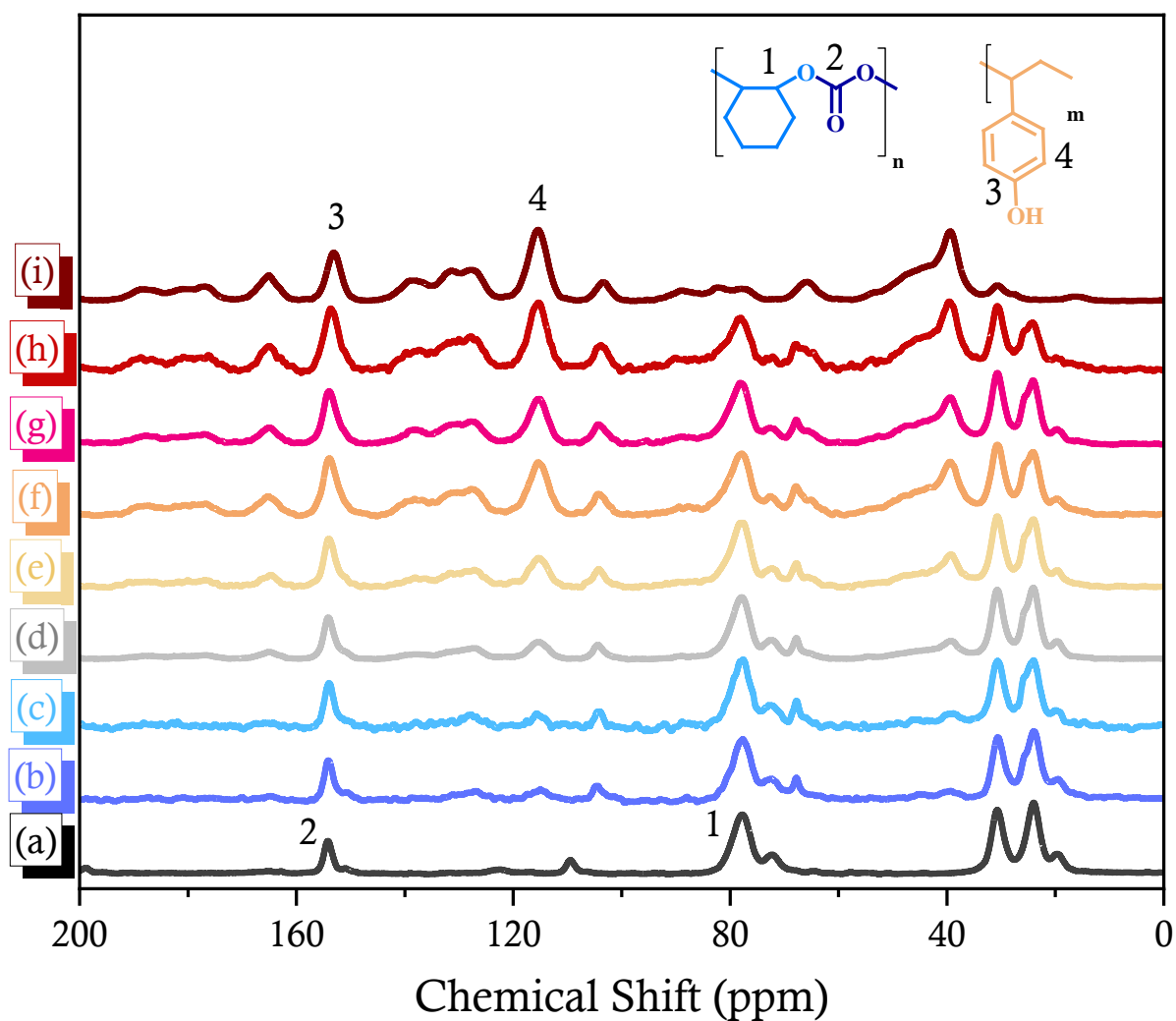


Figure S6: High-resolution solid-state ^{13}C NMR spectroscopy experiment was performed at 25 °C: (a) PCHC, (b) PCHC-80 (c) PCHC-70, (d) PCHC-60, (e) PCHC-50, (f) PCHC-40, (g) PCHC-30, (h) PCHC-20, (i) PVPh

References

1. Thevenon, A.; Garden, J. A.; White, A. J. P.; Williams, C. K. Dinuclear Zinc Salen Catalysts for the Ring Opening Copolymerization of Epoxides and Carbon Dioxide or Anhydrides. *Inorg. Chem.* **2015**, *54*, 11906–11915.