

Supporting Information

Optically Active Porous Materials Constructed by Chirally Helical Substituted Polyacetylene through High Internal Phase Emulsion Approach and the Application in Enantioselective Crystallization

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Experimental section

Materials

Monomer 1 (M1, S isomer), monomer 2 (M2, helical macro-monomer) and monomer 3 (M3), as structurally presented in Figure 1A in the text, were prepared by the reported method.^{1,2} Rhodium catalyst (nbd)Rh⁺B⁻(C₆H₅)₄ (nbd = 2,5-norbornadiene) was synthesized according to the method in literature.³ A bifunctional butynyl ester (dibutynyl adipate) was synthesized following a literature procedure⁴ and was employed as cross-linking agent. Azobisisobutyronitrile (AIBN, Sigma-Aldrich) was purified by recrystallization before use. Butyl acrylate (BA, Beijing Chemical Reagent Co.) was distilled under reduced pressure before use. Trimethylolpropane triacrylate (TMPTA) was purchased from Sigma-Aldrich and used as received. Span-80 was purchased from Beijing Chemical Reagent Co. and used without further purification. Threonine and alanine (D- and L-) were purchased from Aladdin Company (Shanghai, China) and directly used. Solvents were purified by distillation. Deionized water was used for the experiments.

Measurement

Images of the HIPEs were taken with an Olympus BX51M optical microscope. Morphology of the polyHIPEs was observed with a Hitachi S-4800 scanning electron microscope (SEM). FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrophotometer (in KBr tablet). Circular dichroism (CD) and UV-vis absorption spectra were obtained on a Jasco-810 spectropolarimeter. Raman spectra were recorded on a Renishaw inVia-Refl exconfocal Raman microscope with an excitation wavelength of 785 nm. Pore analysis was carried out on a PoreMaster GT 60 mercury

porosimeter. Thermogravimetric analysis (TGA) was carried out with a Q50 TGA at a scanning rate of 10 °C/min under N₂. X-ray diffraction (XRD) analyses were performed with Shimadzu XRD-6000.

Preparation of HIPEs and polyHIPEs

For polyHIPE-1~3 and 6~7, monomer (1 mmol), dibutynyl adipate (10 wt%) and Span-80 (approx. 0.35 mL) were dissolved in CHCl₃ (1.5 mL) and after the solution was cooled down to 0 °C, Rh catalyst (1 wt%) was also dissolved into the solution. Then a given amount of water was added dropwise in the above organic phase at 0 °C under stirring at a rate of 1300 rpm, and subsequently the gel-like HIPE was formed. HIPE-1~3 and 6~7 were heated to 30 °C for 22 h to complete the polymerization to obtain polyHIPEs. For polyHIPE-4~5, monomer (0.227g, the structure unites of M2 was 1 mmol), TMPTA (10 wt%), AIBN (1 wt%) and Span-80 (approx. 0.35 mL) were dissolved in CHCl₃ (1.5 mL) at room temperature (for polyHIPE-5 1 mmol BA was added). Then a given amount of water was added dropwise at room temperature under stirring at a rate of 1300 rpm, and subsequently the HIPE was formed. HIPE-4~5 were heated to 40 °C and maintained at the temperature for 2 h to start pre-polymerization; then the temperature was raised to 55 °C and maintained at that temperature for another 20 h to conduct the polymerization. The resulting products (polyHIPE-1~7) were washed with ethanol repeatedly and dried under vacuum until the weight became constant.

Enantioselective crystallization experiments

Threonine and alanine were used as chiral compound models to conduct enantioselective crystallization. Taking threonine as example, the major procedure is stated below. The crystallization experiment was conducted from the supersaturated solutions of DL-threonine in deionized water at room temperature. 900 mg DL-threonine was added in 3 mL deionized water. The solution was heated to 40 °C under stirring until threonine was completely dissolved. Then a certain amount of polyHIPE (approx. 20 mg, crushed into mm-scaled size) was added in the solution. The mixture was maintained at 40 °C for 10 min and cooled down spontaneously to room

temperature. After 24 h, the crystals were taken out, dried and subjected to characterizations. The obtained crystals (m , mg) were dissolved in deionized water (V , mL) and optical rotation was measured by a polarimeter at room temperature at a wavelength of 589 nm with a standard polarization tube (100 mm long). The enantiomeric excess (e.e.) was calculated according to the following equation:

$$\text{e.e. (\%)} = \frac{10^3 \alpha \cdot V}{m \cdot [\alpha]} \quad (1)$$

where α is the measured optical rotation, $[\alpha]$ is the specific rotation obtained from handbook, m is the mass of crystals, and V is the volume of the solution.

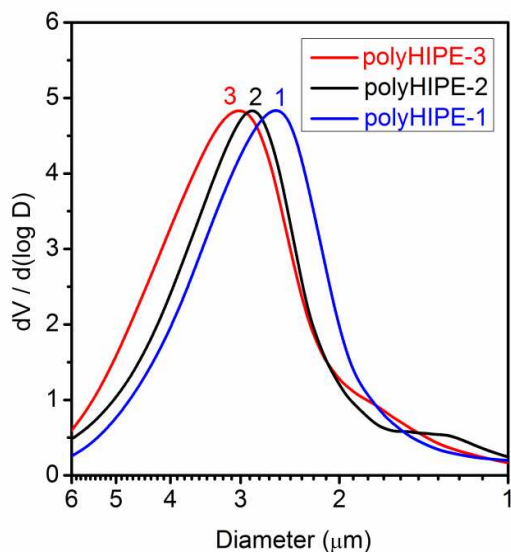


Figure S1. The pore size distribution plots of polyHIPE-1~3.

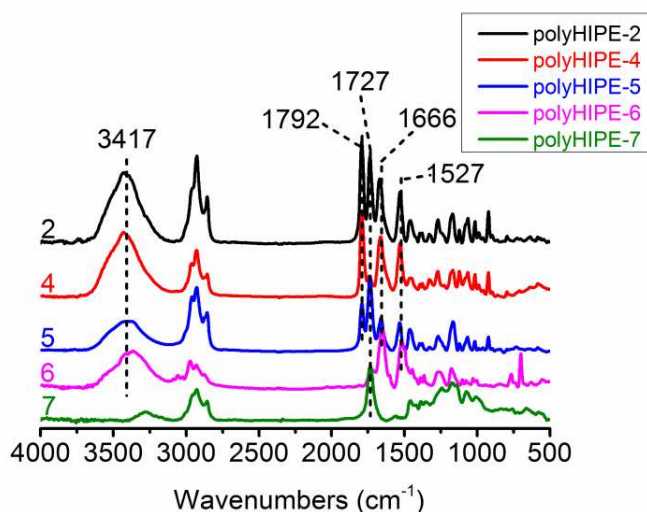


Figure S2. Typical FT-IR spectra of polyHIPE-2 and 4~7 (KBr).

As polyHIPE-1~3 possesses the same chemical structure, they gave the same FT-IR spectra. Herein we only present the spectrum of polyHIPE-2 as representative for polyHIPE-1~3. The absorption peaks at 3417, 1792, 1727, 1666, and 1527 cm^{-1} can be assigned to the N–H stretching vibration, C=O stretching vibration (lactone carbonyl group from M1), C=O stretching vibration (ester group in BA or dibutylene adipate), C=O stretching vibration (amide I) and C–N stretching vibration (amide II), respectively. The C≡C triple bond ($\sim 2100 \text{ cm}^{-1}$) cannot be found in the spectra.

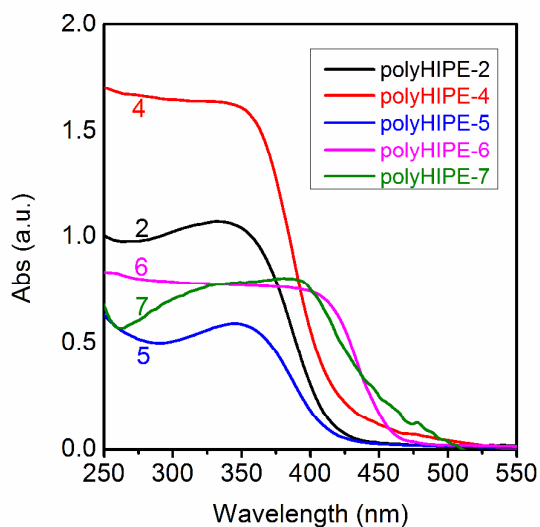


Figure S3. UV-vis spectra of polyHIPE-2 and polyHIPE-4~7 measured by using pressed samples at room temperature.

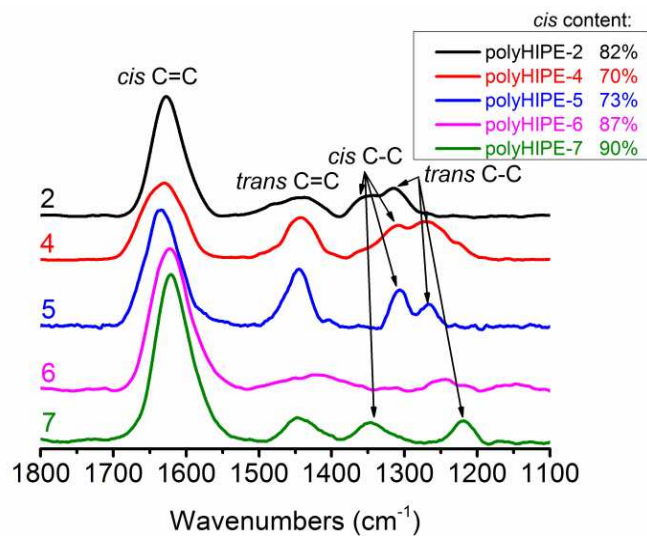


Figure S4. Raman spectra of polyHIPE-2, 4~7 and the *cis* content of polyHIPE-2, 4~7 are 82, 70, 73, 87 and 90%, respectively. (PolyHIPE-2 as representative for polyHIPE-1~3 for they possesses the same chemical structure)

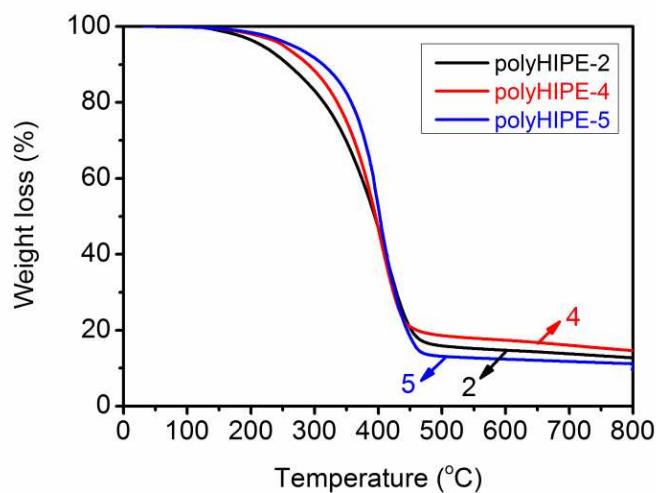


Figure S5. TGA curves of polyHIPE-2, 4~5. Heating at 10 $^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere. (PolyHIPE-1~3 and 6~7 belong to substituted polyacetylene which have similar thermostability, herein we take polyHIPE-2 as an example)

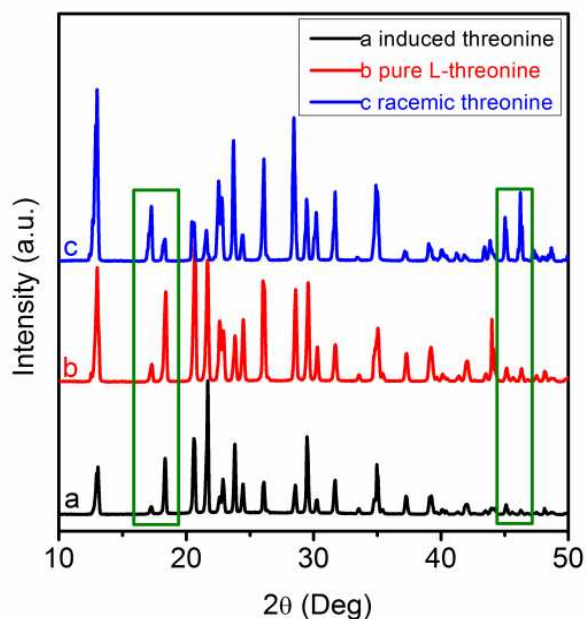


Figure S6. Typical XRD patterns of (a) induced threonine by polyHIPE-2, (b) pure L-threonine, (c) racemic threonine.

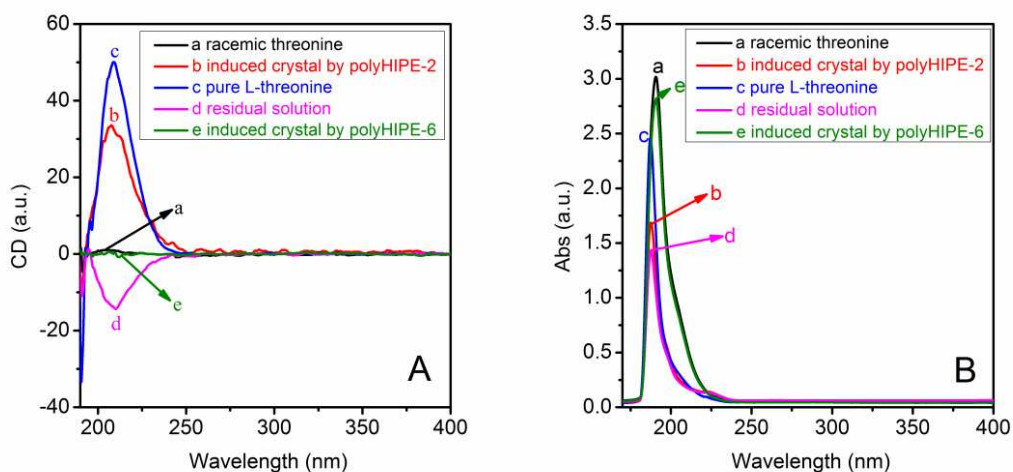


Figure S7. (A) CD and (B) UV-vis spectra of (a) threonine crystals obtained without any additive, (b) threonine crystals induced by polyHIPE-2, (c) pure L-threonine solution, (d) residual solution after removing the threonine crystals induced by polyHIPE-2, and (e) threonine crystals induced by polyHIPE-6. All of the measurements were conducted qualitatively in aqueous solution at room temperature.

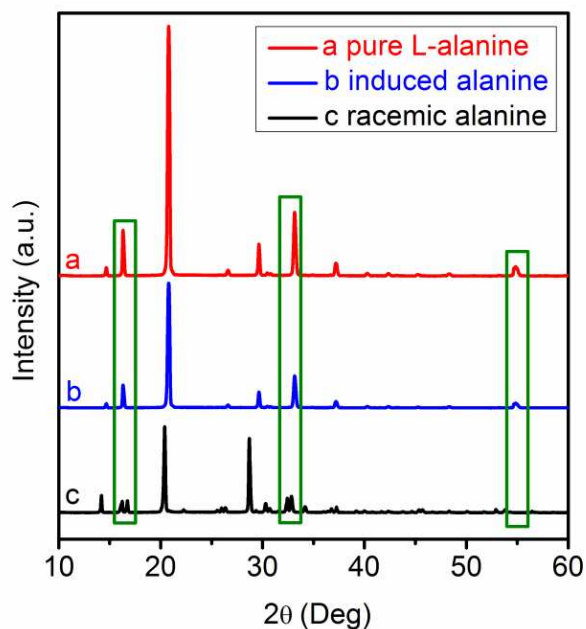


Figure S8. Typical XRD patterns of (a) induced alanine, (b) pure L-alanine and (c) racemic alanine.

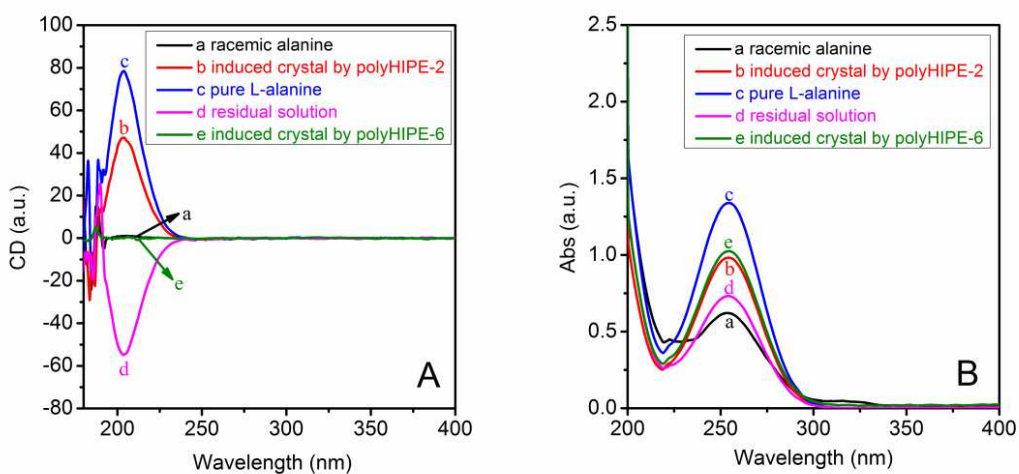


Figure S9. (A) CD and (B) UV-vis spectra of (a) alanine crystals obtained without any additive, (b) alanine crystals induced by polyHIPE-2, (c) pure L-alanine solution, (d) residual solution after removing the alanine crystals induced by polyHIPE-2, and (e) alanine crystals induced by polyHIPE-6. All of the measurements were conducted qualitatively in aqueous solution at room temperature.

Oil adsorption of polyHIPEs

To analyze the swelling ratio of the obtained polyHIPEs, a polyHIPE of known weight (m_0) was placed in a dialysis bag and immersed in an oil at room temperature. After a certain time of adsorption, the wet polyHIPE was taken out and drained for 1 min until no residual droplet was left on the surface. It was weighed (m_t). When the adsorption reached equilibrium, the weight was marked as m_{max} (saturated adsorption). The adsorption capacity was calculated by the following equation, swelling ratio = $(m_t - m_0)/m_0$. The reusability of polyHIPEs was measured as follows: after reaching the m_{max} , the polyHIPE was taken out from the organic liquid and naturally dried for 24 h to exclude all the oil adsorbed previously. When the mass of the polyHIPE was constant and no longer reduced, the polyHIPE was regarded to dry completely. The dried polyHIPE was subjected to the above process for 5 times. In each time the m_{max} was recorded.

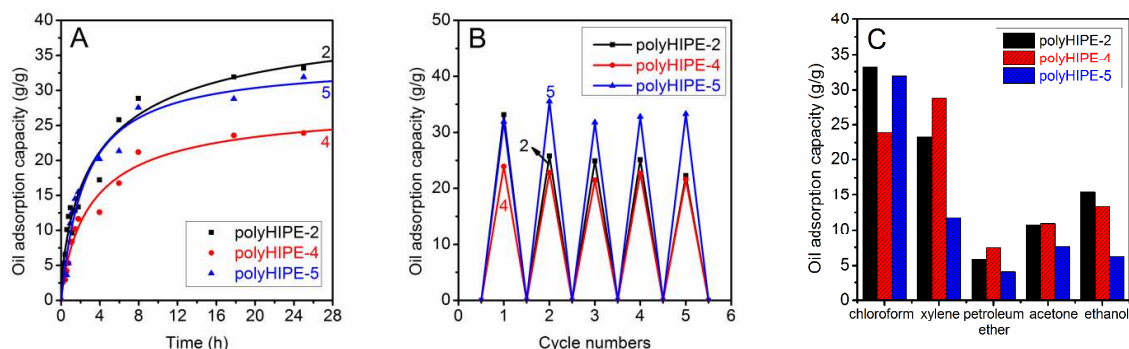


Figure S10. (A) Plots of the oil adsorption capacities of polyHIPE-2, 4 and 5 towards CHCl_3 as a function of adsorption time, (B) the reusability of polyHIPE-2, 4, and 5 in adsorbing CHCl_3 as an example oil and (C) Maximum oil adsorption capacities of polyHIPE 2, 4 and 5 towards five different organic liquids.

The porous structure in theory endows the polyHIPEs with desirable oil absorbability. PolyHIPE-2, 4, and 5 were chosen to conduct oil adsorption experiments for exploring the effects of components (acetylenic and vinylic units) on oil adsorption. As polyHIPE-1~3, 6, and 7 are similar in molecular structure, polyHIPE-2 was selected as the representative. The oil adsorption of polyHIPE-2, 4, and 5 towards CHCl_3 as a function of immersion time is shown in **Figure S10A**. Among the three

examined polyHIPEs, polyHIPE-2 and 5 are superior to polyHIPE-4 in that they possessed not only a faster adsorption rate but also a much larger adsorption capacity. The reusability of polyHIPE-2, 4, and 5 is examined in oil adsorption. The related results are depicted in **Figure S10B**. Excitingly, the oil adsorption processes could be repeated for at least 5 times only with a slight loss in oil adsorption ability. Figure S10B shows us that the reusability of polyHIPE-5 is the best because of butyl acrylate (BA) segment in polyHIPE-5, for BA has been proved to helpfully improve the oil adsorption in literature.⁵ To determine the maximum adsorption capacities of the three polyHIPEs towards more organics, we further conducted oil adsorption tests towards water-immiscible and water-miscible liquids. The former group includes chloroform, xylene, and petroleum ether, while the latter covers acetone and ethanol. The results are shown in **Figure S10C**. The polyHIPEs showed lower oil adsorption ability towards polar organic liquids, i.e. acetone and ethanol due to the weak compatibility between the polyHIPEs and the organic liquids.

Reference

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