

Fabrication of Hierarchically Porous Superhydrophilic Polycaprolactone Monolith Based on Nonsolvent-Thermally Induced Phase Separation

Yu Cao,^a Wenjuan Han,^{*a} Ziyang Pu,^a Xiaofeng Wang,^b Bo Wang,^a Chuntai Liu,^c Hiroshi Uyama,^d Changyu Shen^c

^a*School of Materials Science & Engineering, Zhengzhou University, Zhengzhou 450001, China*

^b*School of Mechanics and Engineering Science, National Center for International Research of Micro-Nano Molding Technology, Key Laboratory of Henan Province for Micro Molding Technology, Zhengzhou 450001, China*

^c*National Engineering Research Center for Advanced Polymer Processing Technology, Zhengzhou University, Zhengzhou 450001, China*

^d*Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, 565-0871, Japan*

**Corresponding author: Wenjuan Han, wenjuan.han@zzu.edu.cn*

Cloud point and phase diagram

The cloud point of PCL-dioxane-ethanol ternary system was determined by cooling the PCL solution from 60 °C with cooling rate at 1 °C/min when the solution become cloudy. The result was shown in Table S1. Compared to PCL concentration, the nonsolvent ratio had an important effect on cloud point.

Table S1. Cloud point temperature in solvent mixture at different PCL concentrations and dioxane/ethanol ratios

Solvent mixture	PCL concentration			
	80 mg/mL	100 mg/mL	120 mg/mL	140 mg/mL
E38/62	—	—	—	—
E30/70	47.0 °C	47.0 °C	47.0 °C	47.0 °C
E27/73	40.5 °C	40.0 °C	40.5 °C	41.0 °C

E25/75	34.0 °C	34.0 °C	33.0 °C	33.0 °C
--------	---------	---------	---------	---------

Cloud point temperature increased as the ethanol ratio decreased, as shown in Figure S1. The cloud point of PCL-dioxane-ethanol ternary system can be calculated with different ethanol concentration (when the PCL concentration is between 80 mg/mL and 140 mg/mL) according to Figure S1.

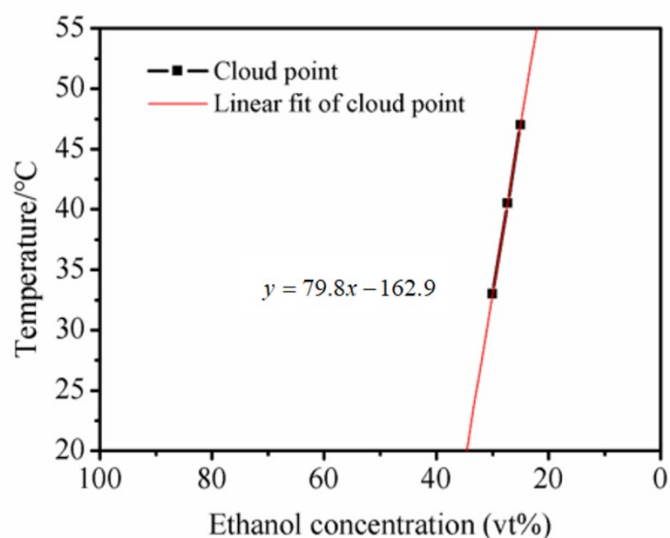


Figure S1. Cloud point temperature curve of PCL-dioxane-ethanol ternary system

The ternary phase diagram was determined as shown in Figure S2. 55 °C and 20 °C was the dissolution temperature and the highest phase separation temperature. In order to meet the conditions of the phase separation, preparation parameters should be selected from range A.

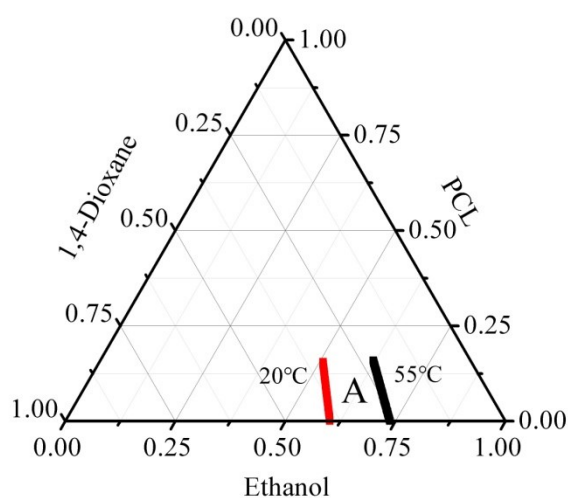


Figure S2. Phase diagram of PCL-dioxane-ethanol ternary system.

The Hansen solubility parameters

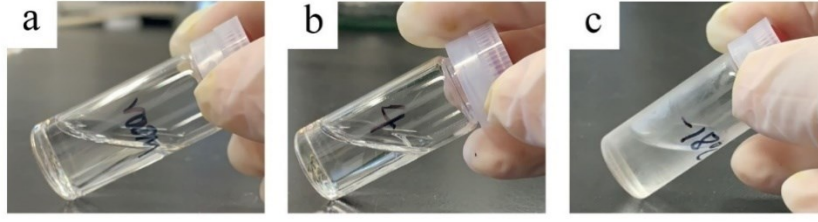


Figure S3 The state of the solvent mixture E30/70 after 24 h at different T_{ps} . (a) 20 °C, (b) 4 °C, (c) -18 °C

The solubility parameters were affected by temperatures. The parameters at different temperatures can be calculated based on the data at 25 °C, and on the thermal expansion coefficient, which was set to 0.0007/K for simplicity. The formulae can be expressed as below^{1, 2}:

$$\delta_d = \delta_{dT} * (1 - \Delta T * \alpha * 1.25) \quad (S1a)$$

$$\delta_p = \delta_{pT} * \left(1 - \Delta T * \frac{\alpha}{2}\right) \quad (S1b)$$

$$\delta_h = \delta_{hT} * \left(1 - \Delta T * \left(0.00122 + \frac{\alpha}{2}\right)\right) \quad (S1c)$$

where δ_d , δ_p , δ_h is respectively dispersion cohesion (solubility) parameter, polar cohesion (solubility) parameter, hydrogen bonding cohesion (solubility) parameter at different temperatures. Accordingly, δ_{dT} , δ_{pT} , δ_{hT} is the parameter at 25 °C, respectively. The ΔT is the change of temperature from 25 °C. And for a solvent mixture, the solubility parameter can also be calculated by formula (S2)^{1, 2}

$$\delta_d = \sum_i \phi_i \delta_{di} \quad (S2a)$$

$$\delta_p = \sum_i \phi_i \delta_{pi} \quad (S2b)$$

$$\delta_h = \sum_i \phi_i \delta_{hi} \quad (S2c)$$

where ϕ_i was volume fraction of each component, δ_{di} , δ_{pi} , δ_{hi} is the parameter of each component respectively.

$$D = \left(4(\delta_{dS} - \delta_{dP})^2 + (\delta_{pS} - \delta_{pP})^2 + (\delta_{hS} - \delta_{hP})^2 \right)^{1/2} \quad (S3)$$

The distance D between the solvent (S) and the solute (P) in the "solubility space" which affected the solubility of polymers in solvents was calculated according to formula (S3)^{1, 2}.

Table S2 PCL solubility parameters at different temperatures

Sample	20 °C			4 °C			-18 °C		
	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h
PCL	17.70	6.20	7.80	17.70	6.20	7.80	17.70	6.20	7.80
Dioxane	18.11	1.81	6.43	18.11	1.81	6.43	18.10	1.81	6.43
Ethanol	15.80	8.80	19.40	15.80	8.80	19.40	15.80	8.80	19.40
E30/70	16.38	7.05	16.16	16.49	6.70	15.51	16.49	6.70	15.51
E25/75	17.85	3.23	10.03	16.38	7.05	16.16	16.38	7.05	16.16

Differential Scanning Calorimetry(DSC)

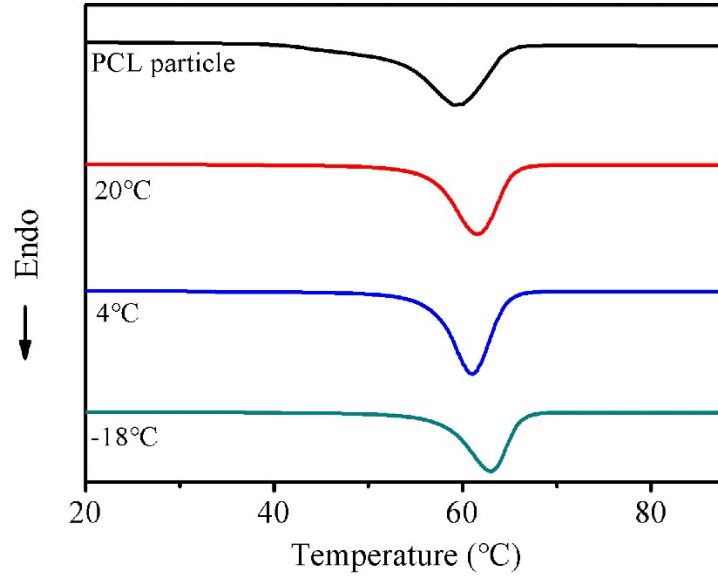


Figure S4. DSC curves of PCL particle and PCL monolith prepared at different cooling temperatures (C_{PCL} of 100 mg/mL, E30/70)

Density

Density of PCL monolith was measured according to ASTM D792-00 involving weighing monolith in water using a sinker. The density of PCL monolith was calculated by formula (S4).^{3, 4}

$$\rho = \frac{a}{a + \omega - b} \rho_{water} \quad (S4)$$

where a was the apparent mass of specimen in air without sinker, b was the apparent mass of specimen and sinker completely immersed in water and ω was the apparent mass of the totally immersed sinker. ρ_{water} was the density of water.

Density of PCL monolith at different phase separation was investigated and the result was shown in Figure S5. Monolith with a T_{ps} of 20 °C had a biggest density, which was 0.20 g/cm³. The density of PCL monolith was 0.18 g/cm³ as the T_{ps} of 4 °C and -18°C. T_{ps} has little effect on density because the mass and volume of monolith was mainly determined by the weight of PCL and the volume of solvent mixture. L-L phase separation occurred from PCL homogeneous solution with the same original volume, so the volume of skeleton was almost the same. Meanwhile, the mass of PCL was the same. Therefore, even though PCL monolith has different structures at different T_{ps} , its density did not differ much.

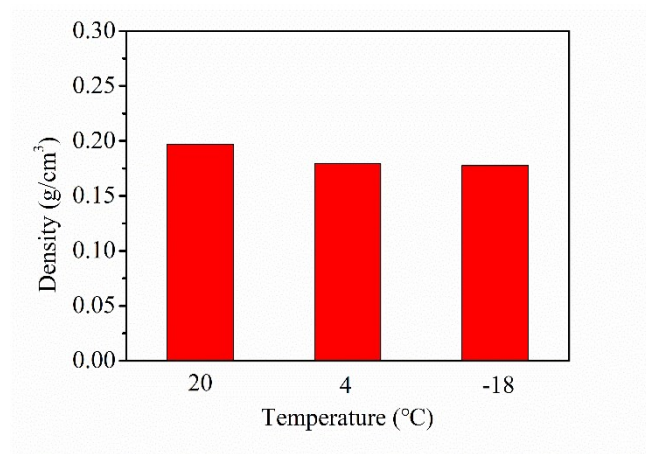


Figure S5. Density of PCL monolith at different phase separation temperatures (E30/70, C_{PCL} was 80 mg/mL)

Mechanical property

Compressive properties were test by compression testing machine (Shimadzu EZ Graph). All samples were cut into a cylindrical shape with a diameter of 12 mm and a height of 10 mm. The compressive rate was set to 1 mm/s. The result was shown in Figure S6. The compressive stress-strain curve of PCL monolith can be divided in two parts. When the strain was relatively small, the stress-strain curve approximated a straight line. When the strain was larger, the stress increased faster, and the slope of the curve increased continuously. Porous structure of monolith had a certain resistance to pressure through shrinkage. When the pressure exceeded the limit that the pore structure can bear, the pore structure would collapse, so the compressive strength increased continuously.

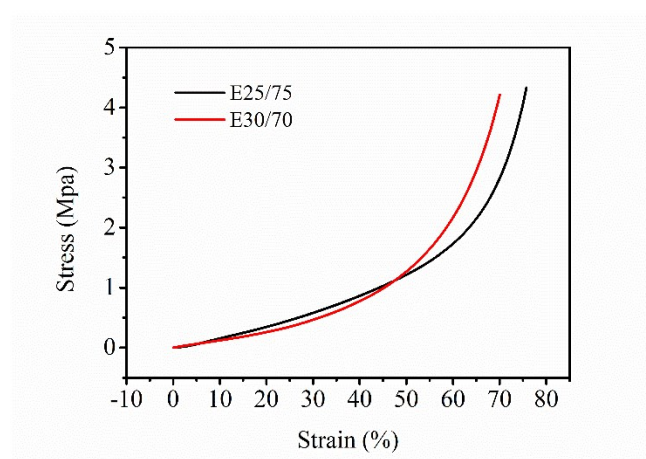


Figure S6. Compressive stress-strain curve of PCL monolith at different ethanol ratios. (T_{ps} at 20 °C, C_{PCL} of 140 mg/mL)

Water uptake

The water uptake was calculated by equation (S5) and the results were shown in Figure S7.

$$\text{Water absorption}(\%) = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{wet}}} \quad (\text{S5})$$

where m_{wet} and m_{dry} were the weight of wet and dry monolith.

The water absorption of PCL monolith and PDA-PCL monolith were 74.18% and 80.36%, respectively. PCL monolith is hydrophobic. After surface modification, the monolith changed to superhydrophilic (Figure 7(d)) due to the hydrophilic of PDA. As a result, the water retention capacity of PDA-PCL monolith was enhanced without significant changes in porous structure (Figure 7(c)).

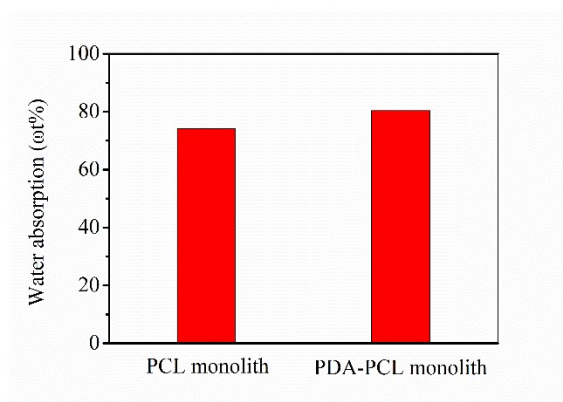


Figure S7. Water absorption of PCL monolith and PDA-PCL monolith

References

1. C. M. Hansen, *Hansen solubility parameters: a user's handbook*, CRC press, 2007.
2. C. Bordes, V. Fréville, E. Ruffin, P. Marote, J. Gauvrit, S. Briançon and P. Lantéri, *International journal of pharmaceutics*, 2010, **383**, 236-243.
3. Z. Xu, X. Jiang, T. Liu, G. Hu, L. Zhao, Z. Zhu and W. Yuan, *The Journal of Supercritical Fluids*, 2007, **41**, 299-310.
4. D. Li, T. Liu, L. Zhao and W. Yuan, *The Journal of Supercritical Fluids*, 2011, **60**, 89-97.