Supporting Information

Fabrication of PVDF ultrafiltration membranes with methyl lactate: enhancing performance through green solvent practices

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 Table S1

 Properties of methyl lactate.

Formula	C4H8O3
Molar mass	$104 \text{ g}\cdot\text{mol}^{-1}$
Appearance	Colorless liquid
Density	1.093 g/cm^3
Melting point	-66 °C
Boiling point	145 °C
Miscibility	Soluble in water and ethanol
Viscosity (23 °C)	3.2 cP

Membrane characterization

The thermal characteristics of PVDF membranes were evaluated using a model Q2000 differential scanning calorimeter (DSC) under a nitrogen atmosphere. Samples underwent heating from room temperature to 200 °C at 10 °C/min, followed by a 5 minute isothermal hold to erase thermal history. Subsequent cooling to 25 °C at 10 °C/min allowed determination of the melting temperature from the endothermic peak during heating.¹

Fourier transform infrared (FTIR) spectra were acquired using a SHIMADZU IRSpirit spectrometer in attenuated total reflection (ATR) mode (400 to 1600 cm⁻¹, 2 cm⁻¹ resolution). X-ray diffraction (XRD) analysis was performed on a Bruker D8 Discover diffractometer (0.02° scanning step). Membrane morphology was examined via GeminiSEM500 scanning electron microscopy (SEM). Cross-sectional samples, prepared by liquid nitrogen freeze-fracturing, and surface samples were gold-sputtered to minimize charging.²

Mechanical properties were measured on a WDW-T600 universal testing machine. All samples were cut into strips with a width of 10 mm and tested at an elongation rate of 100 mm/min.³



Fig. S1 (a) Growth of diluent-rich droplets as temperature decreases. (b) State of the casting solution (PVDF: 17%, Methyl Lactate: 83%) under laser irradiation as a function of temperature. **Solubility Parameters**

Polymer/solvent affinity plays a key role in determining the phase separation process and the subsequent performance of the membrane⁴. In this context, Hansen solubility parameters (HSPs) provide a thermodynamic framework to quantify the empirical "like dissolves like" principle, effectively describing the solubility of polymers. The dispersion forces (δ_D), dipoles (δ_P), and

hydrogen bonding (δ_H) parameters quantify the intermolecular interactions between the solvent and the polymer. ^{5,6} Detailed HSPs can be calculated using Eq. (1).

$$\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} \tag{1}$$

According to the HSPs, the affinity of the polymer for the solvent can also be expressed as R_a , based on Eq. (2). A low R_a value indicates that the polymer and solvent form a homogeneous solution.⁷

$$R_a = \sqrt{4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2}$$
(2)

The relative energy difference (*RED*), defined as R_a/R_0 , serves as a single parameter describing the quality of the solvent and its ability to dissolve the polymer. The *RED* value is used to explain the solubility of a polymer in a given solvent.⁸ While the HSPs of many conventional polymers are well-known, those of new polymers can be easily calculated. The *RED* values are given in Table S2.

When represented visually, δ_D , δ_P , and δ_H are plotted as the x, y, and z coordinates in the Hansen sphere model. This model defines a three-dimensional space where the solubility volume of the polymer is depicted as a sphere with a radius of R_0 , centered at (δ_D , δ_P , and δ_H). R_0 is referred to as the critical radius of interaction for the polymer (Fig. 2a). A polymer-solvent system exhibits good compatibility when the Ra value is low; specifically, if the relative energy difference (*RED*) defined as R_d/R_0 is less than 1, the solvent can effectively dissolve the polymer.⁹ In the Hansen solubility sphere model, solvents capable of dissolving the polymer are represented by green spheres that lie within the Hansen solubility sphere, whereas solvents that cannot dissolve the polymer are depicted as red spheres outside the sphere.⁵



Fig. S2 (a) Hansen solubility sphere radius (R_0) and the position of good and bad solvents for a specific polymer⁸. (b) Hansen solubility sphere for PVDF polymer, indicating compounds that can dissolve the polymer (inside the sphere, green) and those that cannot (outside the sphere, red).

According to the calculations, PVDF is insoluble in methyl lactate at room temperature (Fig. S2b). This result is consistent with previous reports indicating that solubility parameter calculations provide only a rough estimate of solvating power rather than precise measurements.¹⁰

However, the solvating power of methyl lactate for PVDF increases with increasing temperature, enabling PVDF to dissolve and form a clear, homogeneous polymer solution. Upon cooling, gelation occurs. Consequently, these new solvents facilitate the use of the NIPS method in conjunction with the TIPS method for membrane fabrication, similar to other environmentally friendly solvents used in the production of PVDF membranes.

The polymer-solvent interaction parameters were calculated using the Flory-Huggins interaction parameter (χ), expanded by the Hansen solubility parameter using the equation (3):^{10,11}

$$\chi = \frac{V}{RT} \left[(\delta_{D2} - \delta_{D1})^2 + 0.25(\delta_{P2} - \delta_{P1})^2 + 0.25(\delta_{H2} - \delta_{H1})^2 \right]$$
(3)

Here, V represents the solvent's molar volume, δ_D , δ_P and δ_H are the solubility parameters of the polymer and solvent respectively, R denotes the gas constant (8.3145 J mol⁻¹ K⁻¹), and T represents the temperature (368.15K). Lower values of the Flory-Huggins interaction parameter indicate greater compatibility between the polymer and the solvent.

Table S2

Hansen solubility parameters (HSP) of PVDF, methyl lactate, and other selected solvents.

Polymer/solvent	δ_D	δ_P	δ_H	δ	R_{θ}			
blends	(MPa) ^{1/2}	$(MPa)^{1/2}$	$(MPa)^{1/2}$	(MPa) ^{1/2}				
PVDF	17.0	12.1	10.2	23.2	5.0			
	δ_D	δ_P	δ_H	δ	R_a	RED	V	χ
	(MPa) ^{1/2}	$(MPa)^{1/2}$	$(MPa)^{1/2}$	$(MPa)^{1/2}$			cm ³ ·mol ⁻¹	
Methyl lactate	15.5	7.2	7.6	18.7	6.3	1.3	95.50	0.310
DMAC	17.8	14.1	11.8	25.6	3.0	0.6	92.98	0.069
NMP	18.0	12.3	7.2	23.0	3.6	0.72	96.43	0.103
DMF	17.4	13.7	11.3	24.9	2.1	0.42	77.10	0.028





Fig. S3 (a) FTIR spectra of PVDF membranes prepared with varying PEG 200 concentrations. (b) XRD patterns of PVDF membranes prepared with varying PEG 200 concentrations.

PVDF concentration, peak temperature, ΔH_c , and X_c values for PVDF membranes							
Sample	PVDF concentration (wt%)	Peak temp. (°C)	ΔH_c (J/g)	X_{c} (%)			
RP15	15	132.54	42.43	40.60			
RH	17	132.96	34.67	33.18			
RP20	20	133 37	25 40	24 31			

Table S4

Table S3

Sample	PEG concentration (wt%)	Peak temp. (°C)	ΔH_c (J/g)	X_{c} (%)

RE5	5	132.91	33.04	31.62
RE7	7	133.6	27.79	26.59
RH	10	132.96	34.67	33.18

Table S5

Pre-evaporation time, peak temperature, ΔH_c , and X_c values for PVDF membranes

Sample	Pre-evaporation time (s)	Peak temp. (°C)	ΔH_c (J/g)	X_{c} (%)
RH10	10	133.27	31.13	29.79
RH30	30	133.42	28.23	27.01
RH60	60	133.42	39.37	37.67

Table S6

PVDF concentration, porosity, average pore size, and thickness for PVDF membranes

Sample	PVDF /w%	Porosity /%	Average pore size /nm	Thickness /µm
RP15	15%	87.37±2.51	16.04 ± 0.36	80±6
RH	17%	78.02 ± 2.33	9.71±0.12	73±5
RP20	20%	70.14 ± 1.21	14.52±0.19	94±3

Table S7

PEC concentration, porosity, average pore size, and thickness of PVDF membranes

Sample	PEG /w%	Porosity /%	Average pore size /nm	Thickness /µm
RE5	5%	66.84±1.91	9.50±0.13	78±2
RE7	7%	66.68±1.67	9.95±0.16	80±6
RH	10%	78.02 ± 2.33	9.71±0.12	73±5

Table S8

Pre-evaporation time, porosity, average pore size, and thickness of PVDF membranes

Sample	Pre-evaporation time /s	Porosity /%	Average pore size /nm	Thickness /µm
RH10	10	86.56±1.97	21.36±0.42	115±5
RH30	30	79.52±2.09	22.76 ± 0.78	109±3
RH60	60	75.15±3.12	34.81±2.13	105±3

PVDF membrane transparency application

The self-transparency of the ultrafiltration membrane prepared in this experiment, as shown in Fig. S4, is advantageous. The transparent ultrafiltration membrane can be placed directly on a microscope slide due to its high light transmittance, facilitating the observation of surface contaminants using an optical microscope. Light penetrates the transparent membrane from the bottom to the top, allowing simultaneous observation of contaminants on both the top and bottom surfaces. For stained contaminants, the membrane's transparency enables the naked eye to vies both sides of the stain simultaneously.



Fig. S4 Visualization of contaminants in transparent filter membranes using optical microscopy. Analysis of membrane transparency

The transparency of the PVDF membranes cast from methyl lactate is attributed to the uniform and homogeneous distribution of the polymer during the phase inversion process. Firstly, the PVDF molecular chain contains a large number of CF₂ groups, which are uniformly aligned during membrane formation, reducing light scattering.¹⁴ Secondly, the membrane prepared from methyl lactate has a bicontinuous and uniform structure and does not contain a skin layer, which further reduces the scattering and refraction of light, thus improving transparency.

In recent experiments, the addition of propylene carbonate as an additional solvent to the methyl lactate system resulted in a spongy overall cross-section with a spherical crystalline mass at high magnification (Fig. S5b). The increased crystallinity and decreased structural homogeneity of the membrane resulted in increased light scattering and refraction, leading to lower transmittance.¹⁵ Additionally, the inclusion of DMF as a co-solvent produced finger holes in the membrane cross-section (Fig. S5c), dramatically decreasing the membrane's transparency, which once again confirms the effect of membrane structural homogeneity on transparency (Fig. S5d-5g).

Another speculation as to why the transparency of the membrane occurs is based on the cross sectional observation of the membrane prepared by methyl lactate, which seems to be composed of fibers (Fig. S5a). The nanofibers may affect the propagation of light. Theoretically, light is an electromagnetic wave; therefore, visible light can pass through an optical fiber with a diameter of less than 400 nm without reflection or refraction.¹⁶



Fig. S5 SEM images of membranes (a) M1 (PVDF:14%, Methyl lactate:86%), (b) M2 (PVDF:17%, Methyl lactate:43%, Propylene carbonate:40%), and (c) M3 (PVDF:17%,

PEG200:7%, Methyl lactate:38%, DMF:38%). Photos of membranes (d) M1, (e) M2, (f) M3, and (g) M1-M3.



Fig. S6. SEM images of membranes prepared using classical solvents.



Fig. S7. (a) Water contact angles of RP15, RP20 and RH membranes. (b) Water contact angles of RE5, RE7 and RH membranes. (c) Water contact angles of RH10, RH30 and RH60 membranes.



Fig. S8. Tensile strength and elongation at break of PVDF membranes fabricated under different conditions.



Fig. S9. SEM images of the lower cross-sectional areas of the membranes Table S9

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Polymer Solvent		Pure water Flux	BSA rejection	Preparation temperature
		(L/m².h.bar)	(%)	(°C)
PVDF ¹⁷	DES	96.82	96.3	140
PVDF-PSF ¹⁸	PolarClean	162	91.2	130
PVDF-PSF ¹⁸	PolarClean	121	95	130
PVDF ¹⁹	Glyceryl triacetate	99	96.8	200
PVDF	Methyl lactate	135.7±8.2	99.9±0.1	95

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