

Supporting Information for:

Selection Criteria for Solvent and Coagulation Medium to Modulate the Structure of Polymethylmethacrylate Prepared by Wet Phase Inversion




Gustavo Feliciano de Jesus Barcelos ^a, André Santarosa Ferlauto ^b, Kátia Cecília de Souza Figueiredo * ^a

Table S1. Components of the solubility parameters of solvents and their mixtures. Source: Adapted from Barton [16].

Solvent (%v/v)	δ_D (MPa ^{0.5})	δ_P (MPa ^{0.5})	δ_H (MPa ^{0.5})
Acetone	13	9.8	11
Butyl acetate	14.5	7.8	6.8
Butanol	15	10	15.4
Butanone	14.1	9.3	9.5
Chlorobenzene	17.4	9.4	0
Cyclohexanol	13.8	8.6	15.3
Cyclohexanone	15.6	9.4	11
1,4-Dioxane	16.3	10.1	7.9
Ethanol	12.6	11.2	20
Ethyl acetate	13.4	8.6	8.9
Methanol	11.6	13	24
N-hexane	14.9	0	0
N-methylpyrrolidone	16.5	10.4	13.5
Propanol	14.1	10.5	17.7
Tetrahydrofuran	13.3	11	6.7
Water	12.2	22.8	40.4
Acetone (82); Ethanol (18)	12.93	10.05	12.62
Acetone (77); N-heptane (23)	13.53	6.86	8.47
Acetone (20); N-hexane (80)	14.52	1.96	2.2
Acetone (77); N-hexane (23)	13.44	6.86	8.47
Acetone (77); N-octane (23)	13.55	6.86	8.47
Ethyl acetate (20); N-hexane (80)	14.6	1.72	1.78
Water (50); Methanol (50)	11.9	17.9	32.2
Water (5); N-methylpyrrolidone (95)	16.28	11.02	14.84
Water (8); N-methylpyrrolidone (92)	16.16	11.39	15.65
Water (11); N-methylpyrrolidone (89)	16.03	11.76	16.46

Table S2. Detailed conditions for obtaining polymethylmethacrylate membranes with sponge-like structure without the addition of surfactants. Source: Authors

Solvent (%v/v)	Non-solvent (% v/v)	Reference	Detailed experimental conditions
Acetone	Ethanol	[17]	Concentration of polymeric solution: 30% w/v Drying: Immersion in water for 72 hours. 80°C for 48 h. Vacuum for 8 hours. PMMA molar weight: 85,4 kDa Immersion time: 15 minutes
Acetone	Methanol	[13]	Thickness of the polymeric film: 300 µm Concentration of polymeric solution: 14,7% v/v
Acetone	N-hexane	[9]	Thickness of the polymeric film: 300 µm Concentration of polymeric solution: 14,7% v/v; 21% v/v or 29,4% v/v Drying: Vacuum for 24 hours PMMA molar weight: 140 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 60
Acetone	Water	[12]	Thickness of the polymeric film: 300 µm Concentration of polymeric solution: 12,5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature
Acetone	Water	[9]	Thickness of the polymeric film: 300 µm Concentration of polymeric solution: 14,7% v/v; 21% v/v or 29, 4% v/v Drying: Vacuum for 24 hours PMMA molar weight: 140 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 60
Acetone	Water	[18]	Concentration of polymeric solution: 15,15% v/v PMMA molar weight: Mn = 75 kDa; Mw = 84 kDa
Butanone	N-hexane	[9]	Thickness of the polymeric film: 300 µm Concentration of polymeric solution: 14,7% v/v Drying: Vacuum for 24 hours PMMA molar weight: 140 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 60
Butyl acetate	N-hexane	[9]	Thickness of the polymeric film: 300 µm Concentration of polymeric solution: 21% v/v Drying: Vacuum for 24 hours PMMA molar weight: 140 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 60
Chlorobenzene	Ethanol	[6]	Thickness of the polymeric film: 2546,48 µm Concentration of polymeric solution: 6% w/w Drying: Evaporation of solvent and non-solvent for 2 hours PMMA molar weight: 495 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 2 Immersion time: 2 hours
Cyclohexanone	N-hexane	[9]	Thickness of the polymeric film: 300 µm Concentration of polymeric solution: 14,7% v/v Drying: Vacuum for 24 hours PMMA molar weight: 140 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 60
1,4-Dioxane	Butanol	[19]	Thickness of the polymeric film: 300 µm Concentration of polymeric solution: 20% w/w Drying: Freeze drying PMMA molar weight: Mn = 120 kDa Temperature: Room temperature Immersion time: 30 minutes
1,4-Dioxane	Ethanol	[19]	Thickness of the polymeric film: 300 µm Concentration of polymeric solution: 20% w/w Drying: Freeze drying PMMA molar weight: Mn = 120 kDa Temperature: Room temperature

				Immersion time: 30 minutes
				Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 20% w/w Drying: Air drying (3 days, 30 $^{\circ}\text{C}$, relative humidity 70%) or freeze drying
1,4-Dioxane	Methanol	[19]		PMMA molar weight: Mn = 120 kDa Temperature: Room temperature Immersion time: 30 minutes
				Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 20% w/w Drying: Air drying (3 days, 30 $^{\circ}\text{C}$, relative humidity 70%)
1,4-Dioxane	Propanol	[19]		PMMA molar weight: Mn = 120 kDa Temperature: Room temperature Immersion time: 12 or 24 hours
				Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 20% w/w Drying: Freeze drying
1,4-Dioxane	Propanol	[20]		PMMA molar weight: Mn = 120 kDa Temperature: 30 $^{\circ}\text{C}$ Immersion time: 1, 1.5, 2 or 30 minutes
				Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14,7% v/v Drying: Vacuum for 24 hours
Ethyl acetate	N-hexane	[9]		PMMA molar weight: 140 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 60
				Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% w/w Drying: Air drying
N-methylpyrrolidone	N-hexane	[10]		PMMA molar weight: 140 kDa Temperature: Room temperature Immersion time: 10 minutes
				Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.7% v/v
N-methylpyrrolidone	N-hexane	[13]		
				Thickness of the polymeric film: 200 μm Concentration of polymeric solution: 20% w/w Drying: deionized water for 24 h and drying for 24 h at room temperature
N-methylpyrrolidone	Water	[21]		PMMA molar weight: Mw = 90,4 kDa Temperature: Room temperature
				Thickness of the polymeric film: 200 μm Concentration of polymeric solution: 20% w/w Drying: 24 h
N-methylpyrrolidone	Water	[22]		PMMA molar weight: Mw = 90,395 kDa Temperature: Room temperature
				Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.7% w/w Drying: Vacuum for 24 h
Tetrahydrofuran	N-hexane	[9]		PMMA molar weight: 140 kDa Temperature: Room temperature
				Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.7% v/v
Tetrahydrofuran	Water	[13]		
				Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.7% w/w Drying: Vacuum for 24 h
1,4-Dioxane	Methanol (50); Water (50)	[9]		PMMA molar weight: 140 kDa Temperature: Room temperature
				Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.7% w/w Drying: Vacuum for 24 h
Ethyl acetate	Acetone (20); N-hexane (80)	[9]		PMMA molar weight: 140 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 60
				Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.7% w/w Drying: Vacuum for 24 h
Ethyl acetate	Ethyl acetate (20); N-hexane (80)	[9]		

Acetone (82) Ethanol (18)	Water	[12]	<p>PMMA molar weight: 140 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 60</p> <p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% w/w Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature</p>
Acetone (77) N- heptane (23)	N-hexane	[9]	<p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.7% w/w Drying: Vacuum for 24 h PMMA molar weight: 140 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 60</p>
Acetone (77) N- hexane (23)	N-hexane	[9]	<p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.7% w/w Drying: Vacuum for 24 h PMMA molar weight: 140 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 60</p>
Acetone (77) N- octane (23)	N-hexane	[9]	<p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.7% w/w Drying: Vacuum for 24 h PMMA molar weight: 140 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 60</p>

Table S3. Detailed conditions for obtaining polymethylmethacrylate membranes with finger-like structure without the addition of surfactants. Source: Authors

Solvent (%v/v)	Non-solvent (% v/v)	Reference	Detailed experimental conditions
Acetone	Water	[23]	<p>Concentration of polymeric solution: 20% w/w Temperature: 25-28 °C</p>
Butyl acetate	N-hexane	[11]	<p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.5% w/w Drying: Air drying PMMA molar weight: 140 kDa</p>
Butyl acetate	N-hexane	[9]	<p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.7% v/v Drying: Vacuum for 24 h PMMA molar weight: 140 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 60</p>
Cyclohexanol	Water	[24]	<p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 20% w/w Drying: Freeze drying PMMA molar weight: Mw = 10.1 kDa; Mn = 48,3 kDa Temperature: 70 °C Non-solvent/solution volume ratio: 60 Immersion time: 15 hours</p>
1,4-Dioxane	Water	[13]	<p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.7% v/v</p>
N-methylpyrrolidone	Water	[10]	<p>Thickness of the polymeric film: 300, 500 or 2000 μm Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Immersion time: 10 minutes</p>
N-methylpyrrolidone	Water	[11]	<p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.5% w/w Drying: Air drying PMMA molar weight: 140 kDa Immersion time: 10 minutes</p>
N-methylpyrrolidone	Water	[9]	<p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.7%, 21% or 29.4% v/v</p>

N-methylpyrrolidone	Water	[25]	<p>Drying: Vacuum for 24 hours PMMA molar weight: 140 kDa Temperature: Room temperature Non-solvent/solution volume ratio: 60</p> <p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 15% or 20% v/v Drying: Air drying Temperature: Room temperature</p>
N-methylpyrrolidone (95) Water (5)	Water	[25]	<p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 15% or 20% v/v Drying: Air drying Temperature: Room temperature</p>
N-methylpyrrolidone (92) Water (8)	Water	[25]	<p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 15% or 20% v/v Drying: Air drying Temperature: Room temperature</p>
N-methylpyrrolidone (89) Water (11)	Water	[25]	<p>Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 15% v/v Drying: Air drying Temperature: Room temperature</p>

Table S4. HLB (Hypophilic-Lipophilic Balance) Index of Surfactants. Source: Lin and coauthors [12]

Surfactant	HLB
Brij 35	16.9
Span 20	8.6
Span 40	6.7
Span 80	4.3
Span 85	1.8
Tween 20	16.7
Tween 80	15.0
Tween 85	11.0

Table S5. Detailed conditions for obtaining polymethylmethacrylate membranes with sponge-like structure with the addition of surfactants. Source: Authors

Surfactant (%v/v)	Non-solvent (% v/v)	Reference	Detailed experimental conditions
Brij 35	N-hexane	[12]	<p>Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature</p>
Span 20	Water	[12]	<p>Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature</p>
Span 40	Water	[12]	<p>Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature</p>
Span 80	Water	[12]	<p>Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% v/v</p>

				Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature
Span 85	Water	[12]		Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μ m Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature
Tween 20	N-hexane	[11]		Solvent: Butyl acetate Concentration of surfactant: 8.9% v/v Thickness of the polymeric film: 300 μ m Concentration of polymeric solution: 14.5% w/w Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature
Tween 20	N-hexane	[12]		Solvent: acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μ m Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature
Tween 80	N-hexane	[12]		Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μ m Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature
Tween 80	N-hexane	[10]		Solvent: Acetone Concentration of surfactant: 18% v/v Thickness of the polymeric film: 300 μ m Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Immersion time: 10 minutes
Tween 80	N-hexane	[11]		Solvent: Acetone Concentration of surfactant: 1.8% or 18% v/v Thickness of the polymeric film: 300 μ m Concentration of polymeric solution: 14.5% w/w Drying: Air drying PMMA molar weight: 140 kDa Immersion time: 10 minutes
Tween 85	N-hexane	[12]		Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μ m Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature

Table S6. Detailed conditions for obtaining polymethylmethacrylate membranes with finger-like structure with the addition of surfactants. Source: Authors

Surfactant (%v/v)	Non-solvent (% v/v)	Reference	Detailed experimental conditions
Brij 35	Water	[12]	Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature
Span 20	N-hexane	[12]	Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature
Span 40	N-hexane	[12]	Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature
Span 80	N-hexane	[12]	Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature
Span 80	Water	[11]	Solvent: N-methylpyrrolidone Concentration of surfactant: 18% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.5% w/w Drying: Air drying PMMA molar weight: 140 kDa Immersion time: 10 minutes
Span 85	N-hexane	[12]	Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature
Tween 20	Water	[12]	Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature
Tween 80	Methanol	[11]	Solvent: Acetone Concentration of surfactant: 18% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.5% w/w Drying: Air drying PMMA molar weight: 140 kDa Immersion time: 10 minutes
Tween 80	Water	[12]	Solvent: Acetone Concentration of surfactant: 1.8%, 3.6%, 8.9% or 18% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature
Tween 80	Water	[12]	Solvent: Acetone (82% v/v) Ethanol (18% v/v) Concentration of surfactant: 1.8% v/v Thickness of the polymeric film: 300 μm

				<p>Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature</p>
Tween 80	Water	[11]		<p>Solvent: Acetone Concentration of surfactant: 1.8% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.5% w/w Drying: Air drying PMMA molar weight: 140 kDa Immersion time: 10 minutes</p>
Tween 80	Water	[11]		<p>Solvent: Acetone Concentration of surfactant: 18% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 14.5% w/w Drying: Air drying PMMA molar weight: 140 kDa Immersion time: 2 seconds or 10 minutes</p>
Tween 80	Water	[10]		<p>Solvent: Acetone Concentration of surfactant: 18% v/v Thickness of the polymeric film: 500 μm or 2000 μm Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Immersion time: 10 minutes</p>
Tween 85	Water	[12]		<p>Solvent: Acetone Concentration of surfactant: 3.6% v/v Thickness of the polymeric film: 300 μm Concentration of polymeric solution: 12.5% v/v Drying: Air drying PMMA molar weight: 140 kDa Temperature: Room temperature</p>
