Supplementary Information

Thymol: Nature's solvent for sustainable hollow fiber fabrication

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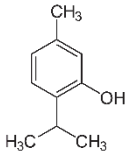
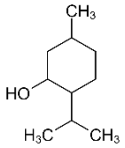
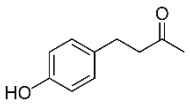
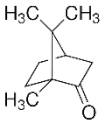
Table S1. Physicochemical properties of the deep eutectic solvent components.

	Component A	**Component B**		
	Thymol	**DL-Menthol**	**Raspberry Ketone**	**Camphor**
Chemical Formula	$C_{10}H_{14}O$	$C_{10}H_{20}O$	$C_{10}H_{12}O_2$	$C_{10}H_{16}O$
Chemical structure				
Molar mass (g mol^{-1})	150.22	156.27	164.20	152.24
Boiling temperature (˚C)	232	216	140 – 146	204
Melting temperature (˚C)	49 – 51	34 – 36	82 – 84	175 – 177
Density (g mL^{-1} at 25 ˚C)	0.965	0.890	1.046	0.992
Solubility in water (g L^{-1} at 25 ˚C)	0.98	0.42	0.15	1.25

https://www.sigmaaldrich.com/SA/en; https://pubchem.ncbi.nlm.nih.gov/

Table S2. Effect of deep eutectic solvents components molar ratio on the solubilization of Ultem®.

Component A	Component B	Ratio (mol/mol)	Solubilization of 13 wt% Ultem®
Thymol	DL-Menthol	4:1	Yes
		1:1	Yes (>48 h)
		1:4	No
	Raspberry Ketone	4:1	Yes
		1:1	No
		1:4	No
	Camphor	4:1	Yes
		1:1	No
		1:4	No

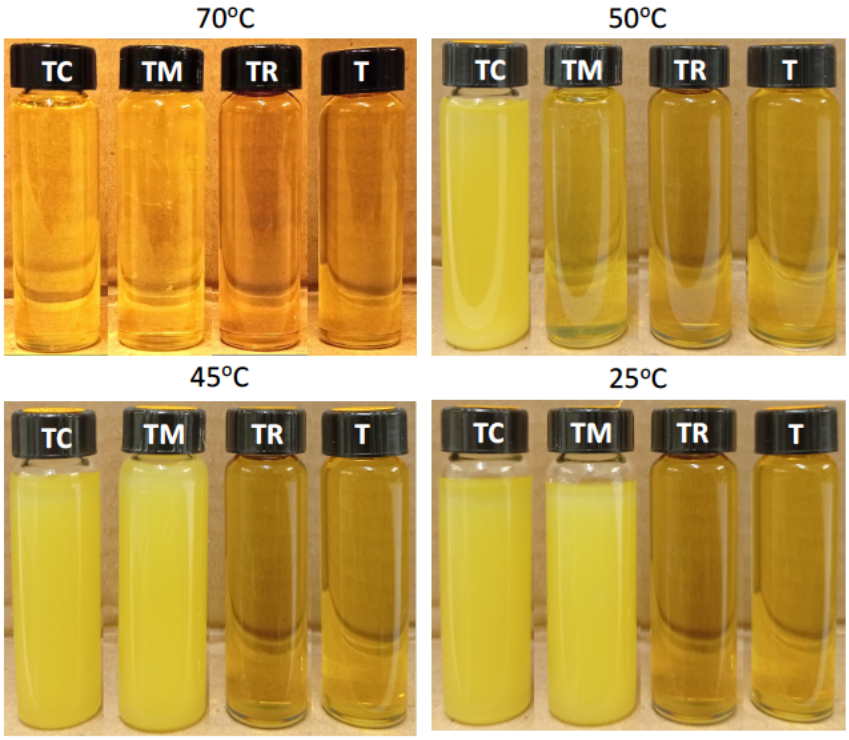
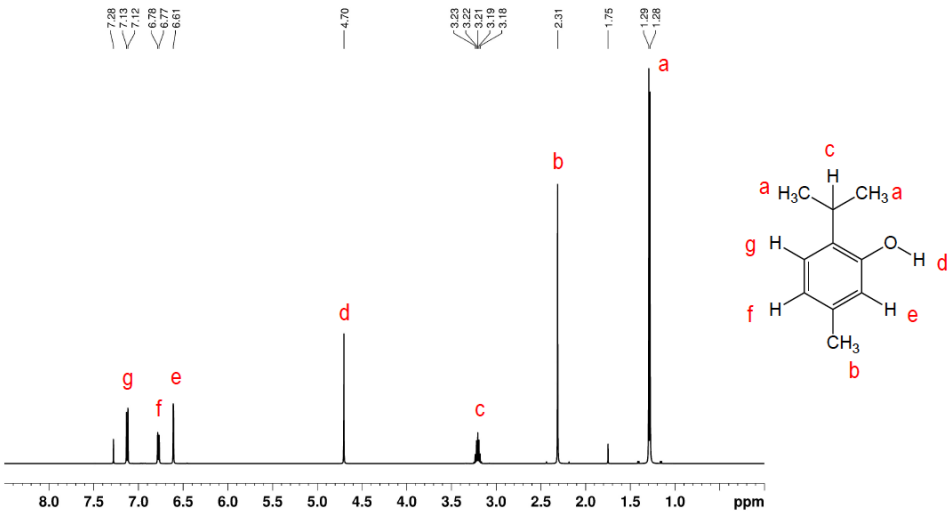
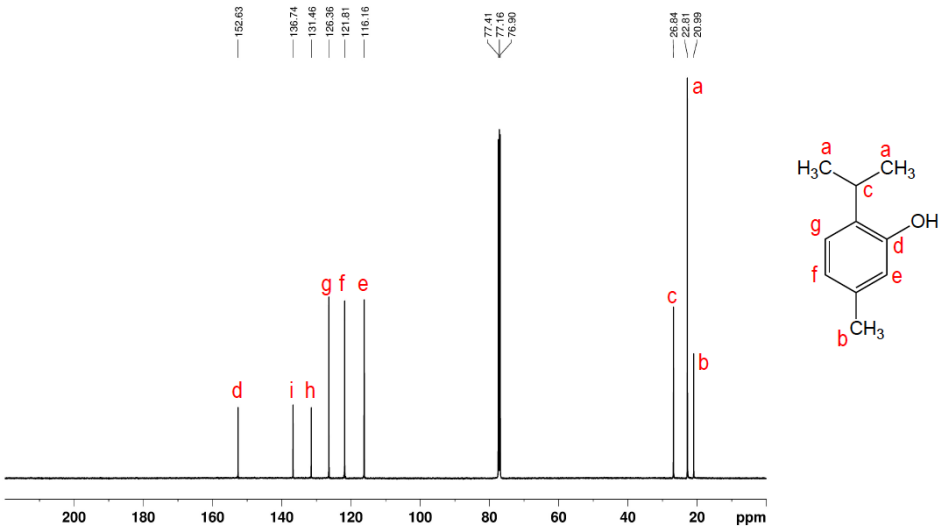


Figure S1 Solubilization of 13 wt% Ultem®. 4:1 (molar) thymol/camphor (TC), thymol/menthol (TM), thymol/raspberry ketone (TR) and pure thymol (T) at various temperatures.



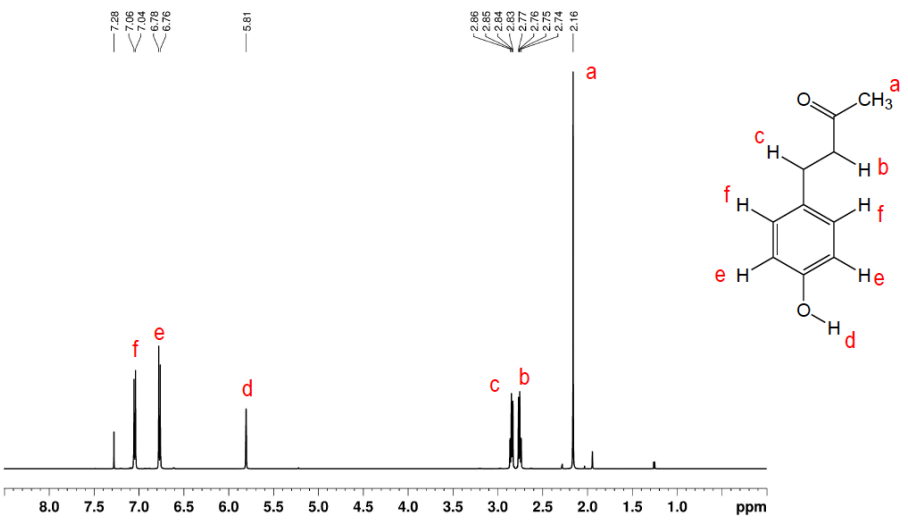
^{1}H NMR	H_a	H_b	H_c	H_d	H_e	H_f	H_g
δ (ppm)	1.29	2.31	3.21	4.70	6.61	6.78	7.13
Area	6	3	1	1	1	1	1
Multiplicity	d	s	hep.	s	s	d	D
Couplings	$^3J_{ac}$ = 7 Hz and $^3J_{fg}$ (ortho) = 8 Hz						

Figure S2. Spectroscopic analysis of thymol. 600MHz ^{1}H NMR spectrum with peak assignments.



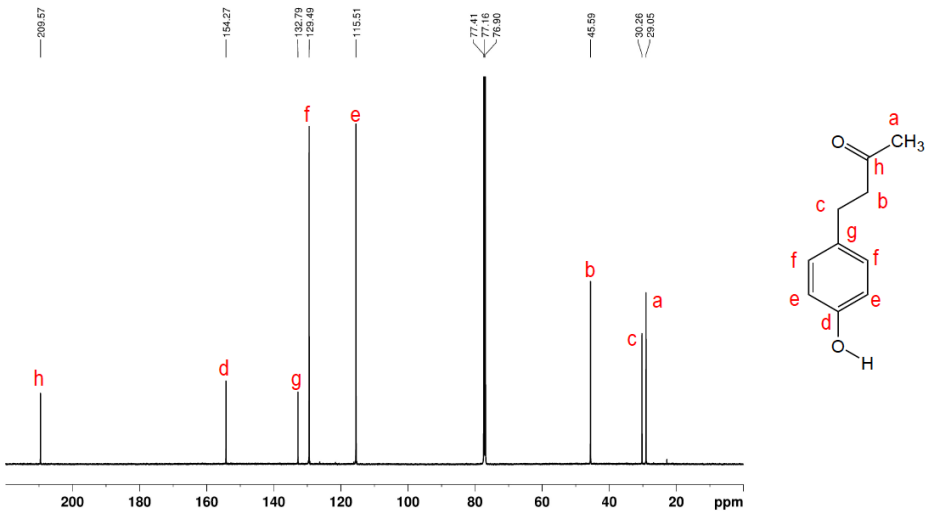
^{13}C NMR	C_a	C_b	C_c	C_d	C_e	C_f	C_g	C_h	C_i
δ (ppm)	22.81	20.99	26.84	152.6	116.2	121.8	126.4	131.5	136.7

Figure S3. Spectroscopic analysis of thymol. 600MHz ^{13}C NMR spectrum with peaks assignments.



^{1}H NMR	H_a	H_b	H_c	H_d	H_e	H_f
δ (ppm)	2.16	2.76	2.85	5.81	6.77	7.05
Area	3	2	2	1	2	2
Multiplicity	s	t	t	s	d	d
Couplings	$^3J_{bc}$ = 7.3 Hz and $^3J_{ef}$ (ortho) = 8.5 Hz					

Figure S4. Spectroscopic analysis of raspberry ketone. 600 MHz ^{1}H NMR spectrum with peak assignments.



^{13}C NMR	C_a	C_b	C_c	C_d	C_e	C_f	C_g	C_h
δ (ppm)	29.05	45.59	30.26	154.3	115.5	129.5	132.8	209.6

Figure S5. Spectroscopic analysis of raspberry ketone. The 600MHz ^{13}C NMR spectrum with peaks assignments.

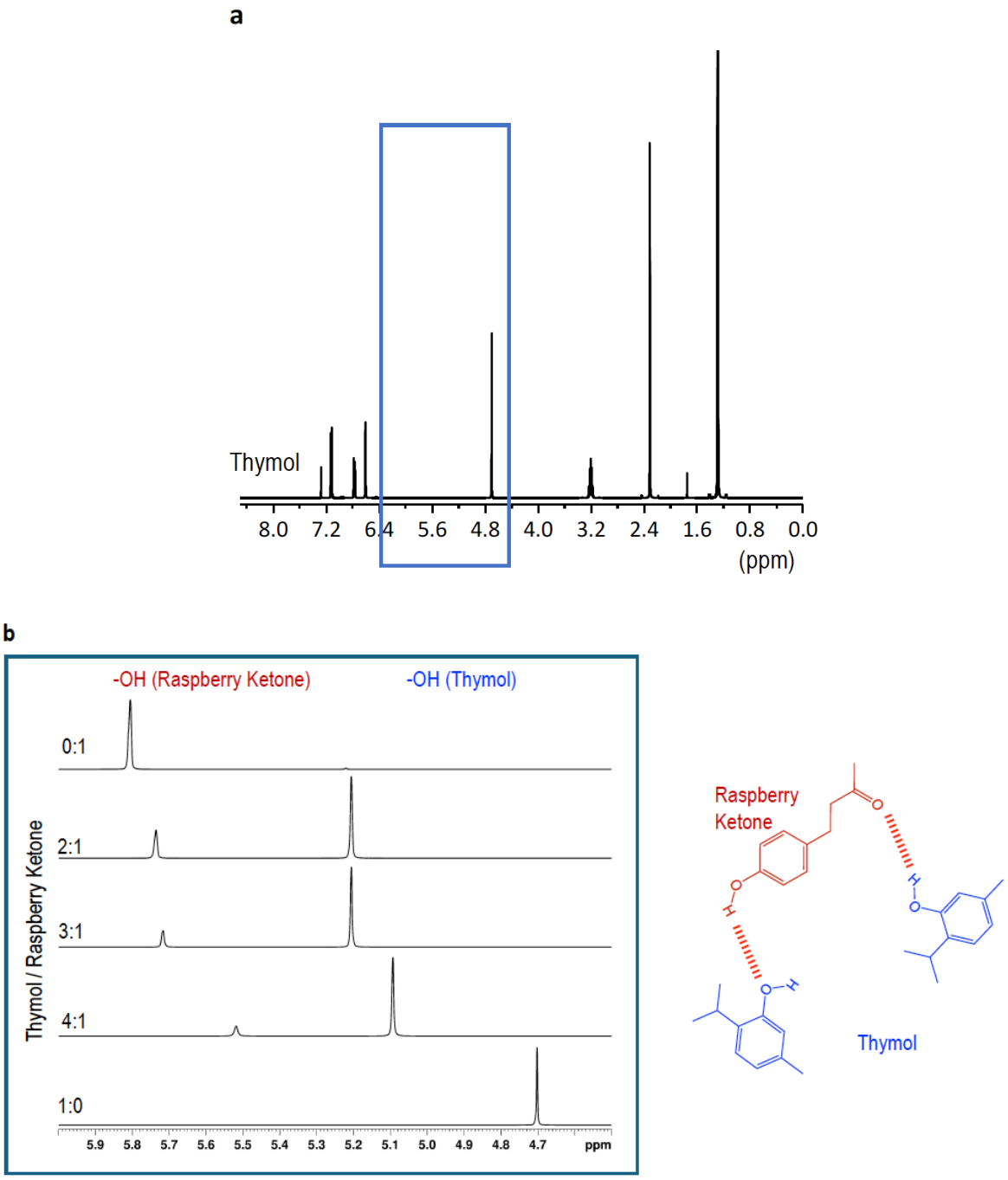


Figure S6. Deep eutectic solvents spectroscopic analysis. ^{1}H NMR spectra: **a**, Thymol in $CDCl_3$ (0-8 ppm). **b**, Peaks relative to OH groups of thymol (4.6-5.3 ppm) and raspberry ketone (5.3-5.9 ppm) mixed in different ratios and scheme of H-bond interactions.

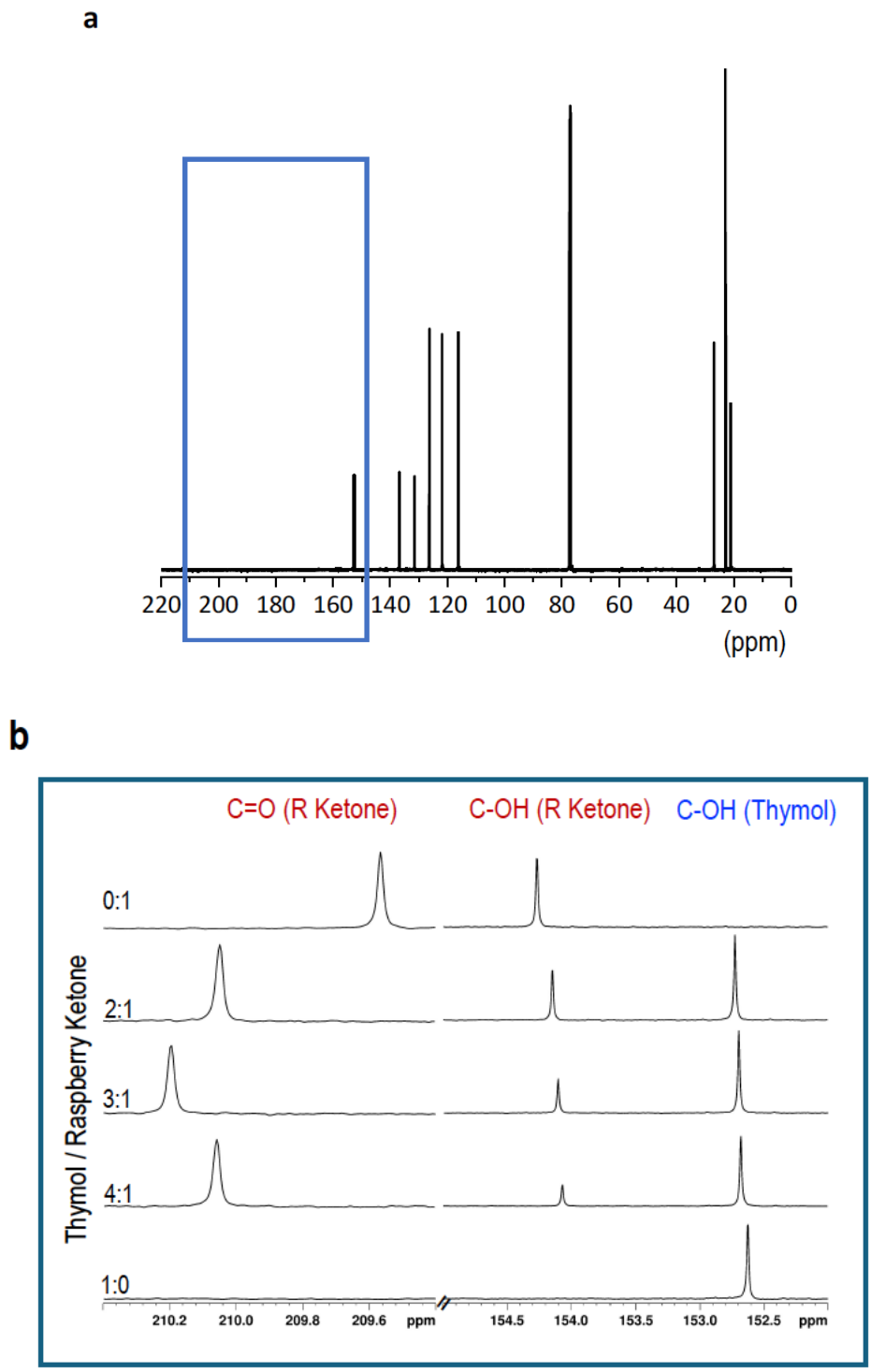


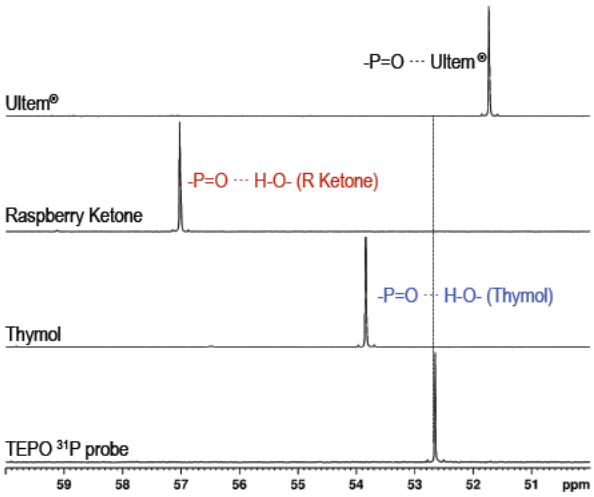
Figure S7. Deep eutectic solvents spectroscopic analysis. ^{13}C NMR spectra. **a**, Thymol in $CDCl_3$ (0-220 ppm). **b**, Peaks relative to C-OH groups of thymol (152-153 ppm) and raspberry ketone (153-155 ppm), and C=O group of raspberry ketone (209.4-210.3 ppm) for mixtures of different component ratios.

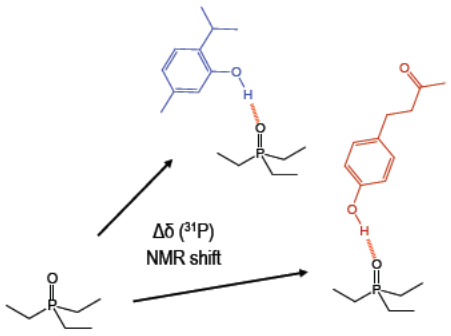
Table S3. Spectroscopic analysis. ^{1}H NMR and ^{13}C NMR chemical shifts for Ultem®, thymol, raspberry ketone, and mixtures therefrom.

^{1}H NMR (4.6-6.3 ppm)	**Thymol**		**Raspberry Ketone**	
	–OH (ppm)	Δδ (ppm)	–OH (ppm)	Δδ (ppm)
Thymol	4.70	-	-	-
Raspberry Ketone	-	-	5.81	-
1:1 Thymol/ Raspberry Ketone	5.51	0.81	6.21	0.41
2:1 Thymol/ Raspberry Ketone	5.21	0.50	5.74	-0.07
3:1 Thymol/ Raspberry Ketone	5.21	0.50	5.72	-0.09
4:1 Thymol/ Raspberry Ketone	5.09	0.39	5.52	-0.29
Ultem® in Thymol	5.06	0.36	-	-
Ultem® in 4:1 Thymol/ Raspberry Ketone	5.04	0.33	5.40	-0.41

^{13}C NMR (152-211 ppm)	**Thymol**		**Raspberry Ketone**			
	C–OH (ppm)	Δδ (ppm)	C–OH (ppm)	Δδ (ppm)	C=O (ppm)	Δδ (ppm)
Thymol	152.63	-	-	-	-	-
Raspberry Ketone	-	-	154.27	-	209.57	-
1:1 Thymol/ Raspberry Ketone	152.79	0.16	154.23	-0.03	210.37	0.80
2:1 Thymol/ Raspberry Ketone	152.73	0.10	154.15	-0.12	210.05	0.48
3:1 Thymol/ Raspberry Ketone	152.70	0.07	154.10	-0.16	210.20	0.63
4:1 Thymol/ Raspberry Ketone	152.68	0.05	154.07	-0.20	210.06	0.49
Ultem® in Thymol	152.60	0.02	-	-	-	-
Ultem® in 4:1 Thymol/ Raspberry Ketone	152.71	0.09	154.10	-0.16	209.48	-0.08

^{13}C NMR (112-167 ppm)	**Ultem®**			
	C–O (ppm)	Δδ (ppm)	C=O (ppm)	Δδ (ppm)
Ultem®	152.77	-	166.51	-
Ultem® in Thymol	152.71	-0.06	166.84	0.32
Ultem® in 4:1 Thymol/ Raspberry Ketone	152.75	-0.03	166.67	0.15





31P NMR	Signal (ppm)	Δδ (31P)
TEPO Probe	52.65	-
TEPO + Thymol	53.84	1.19
TEPO + Raspberry Ketone	57.02	4.37
TEPO + Ultem®	51.73	-0.92

Figure S8. Hydrogen bond donor-acceptor spectroscopic analysis. ^{31}P NMR spectra of triethyl phosphine oxide (TEPO) mixed with Ultem®, raspberry ketone or thymol.

Hansen solubility parameters

To theoretically predict the solubility of Ultem® in various solvents, the Hansen solubility parameters and the solubility parameter distance R_a were estimated. Initially, the Hansen solubility parameters of the various individual compounds (δ) and the mixtures (δ_M^{mix}) were calculated as shown in equations 1 and 2 respectively.

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (1)$$

where δ_D, δ_P and δ_H were the components of the Hansen solubility parameter related to the dispersive, dipole-dipole and hydrogen bonding interactions, respectively.

$$\delta_M^{mix} = \alpha\delta_M^1 + (1-\alpha)\delta_M^2 \quad (2)$$

where δ_M^1 or δ_M^2 could be δ_D, δ_P or δ_H of components 1 or 2 and α was the volume fraction of component 1.

The similarity of a potential solvent (component 1) and the polymer (component 2) was quantified by evaluating the solubility parameter distance, R_a, as per the following equation 3.

$$R_a = \sqrt{[4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2]} \quad (3)$$

Critical Entanglement Concentration (*C) calculation**

To experimentally understand the appropriate solvents for preparing dope solutions, diluted Ultem® solutions (0.05, 0.1 and 0.2 w/v %) were prepared in DES, thymol, NMP and DMF. Their relative and reduced viscosities were measured at 25°C (for DES, NMP and DMF) and at 50°C (for thymol) using an Ubbelohde viscometer (Lauda iVisc, Germany). The intrinsic viscosity [η] of the polymer solutions were calculated from the measured viscosities (at different polymer concentrations) by the following equation:

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta_{rel} - 1}{C} \right) = \lim_{c \to 0} \eta_{red} \quad (4)$$

where *C* is the concentration of the polymer solution

$$\text{relative viscosity, } \eta_{rel} = \frac{polymer\ solution\ dynamic\ viscosity}{solvent\ dynamic\ viscosity} \quad (5)$$

$$\text{reduced viscosity, } \eta_{red} = \frac{\eta_{rel} - 1}{C} \quad (6)$$

The concentration at which the polymer coils start to entangle, C^*, was further calculated from the intrinsic viscosity by the following equation:

$$C^* = \frac{1}{\eta} \quad (7)$$

Table S4. Theoretical calculations of Hansen solubility parameters[1,2].

Component	Molar mass (g mol^{-1})	Density (g mL^{-1}) at 25°C	Hansen Solubility Parameter (MPa$^{1/2}$)				R_a of Ultem® with solvents
			Dispersion (δ_d)	Polarity (δ_p)	H-bonding (δ_h)	Total (δ)	
Ultem®	606.67	1.27	21.1	6.7	8.1	23.6	-
Thymol	150.22	0.96	19.0	4.5	10.8	22.3	5.5
DL-Menthol	156.27	0.89	16.6	4.7	10.6	20.2	9.6
D-Camphor	152.24	0.99	17.8	9.4	4.7	20.7	7.9
Raspberry Ketone	164.20	1.03	18.7	7.6	9.7	22.4	5.1
NMP	99.13	1.03	18.0	12.3	7.2	23.0	8.4
DMF	73.10	0.94	17.4	13.7	11.3	24.9	10.7
DMSO	78.13	1.10	18.4	16.4	10.2	26.7	11.3
DMAc	87.12	0.94	16.8	11.5	10.2	22.8	10.1
4:1 Thymol/ DL-Menthol	156.27	0.95	18.5	4.5	10.8	21.9	6.3
4:1 Thymol/ Camphor	152.24	0.97	18.8	5.5	9.6	21.8	5.1
4:1 Thymol/ Raspberry Ketone	164.20	0.97	18.9	5.1	10.6	22.3	5.2

$R_a{}^2 = 4(\Delta\delta_d)^2 + \left(\Delta\delta_p\right)^2 + (\Delta\delta_h)^2$

[1]Hansen CM. Hansen solubility parameters: a user's handbook. CRC press (2007).

[2]Chung, T.-S. and Z.-L. Xu, J. Membr. Sci., 1998, 147, 35-47.

NMP: N-methyl pyrrolidone; DMF: N, N-dimethyl formamide; DMSO: dimethyl sulfoxide; DMAc: dimethyl acetamide.

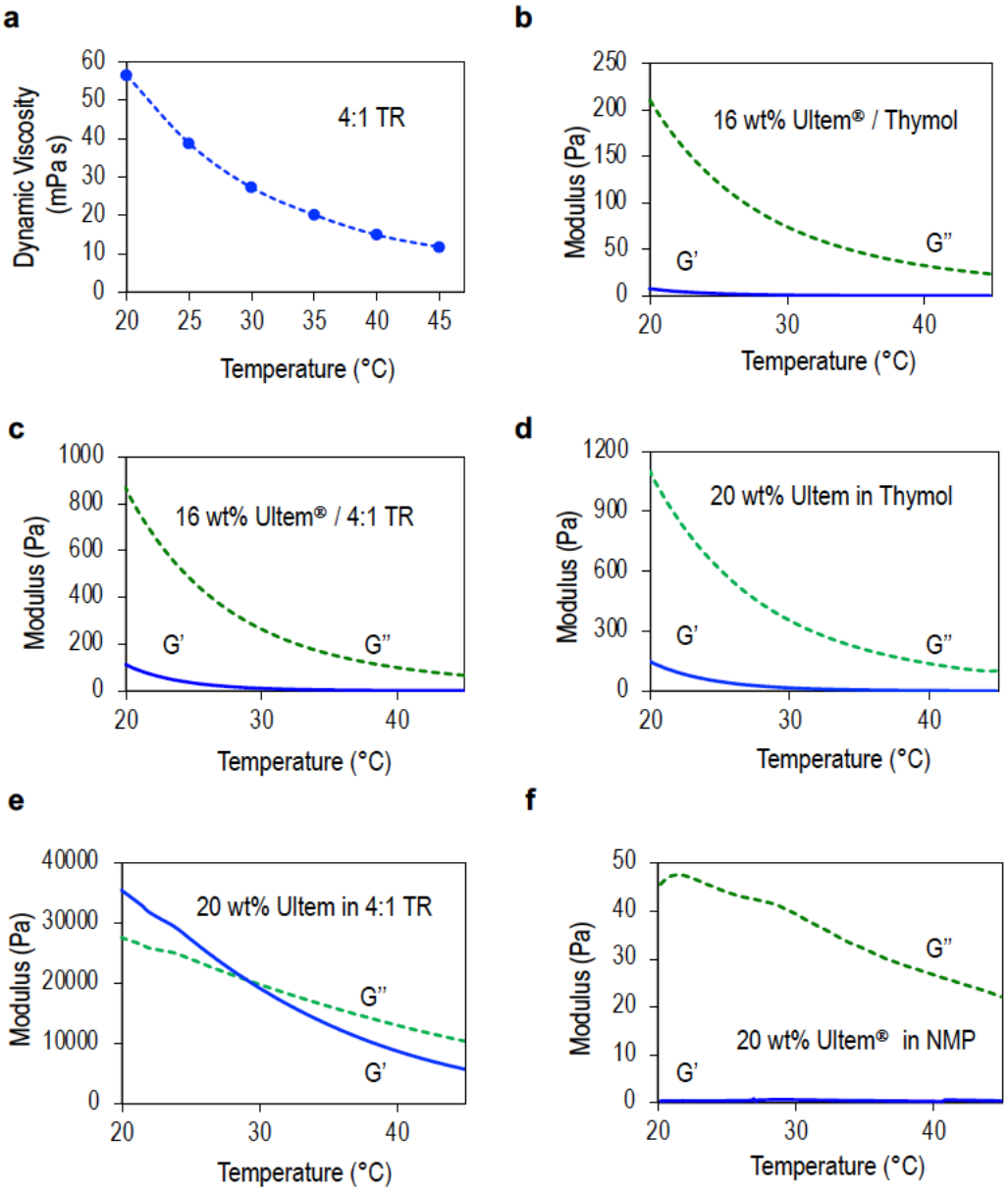
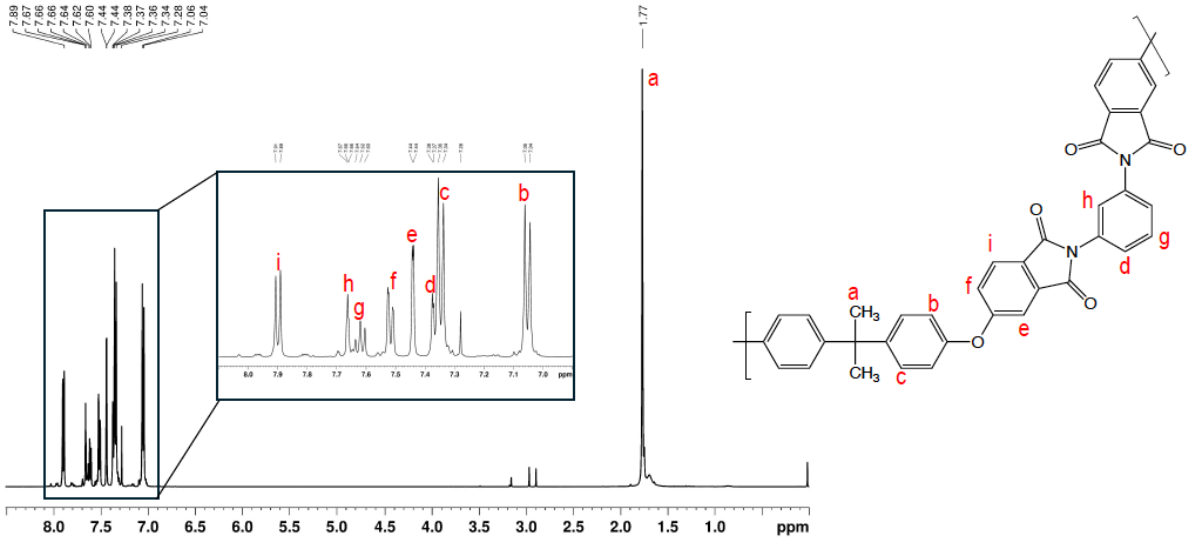
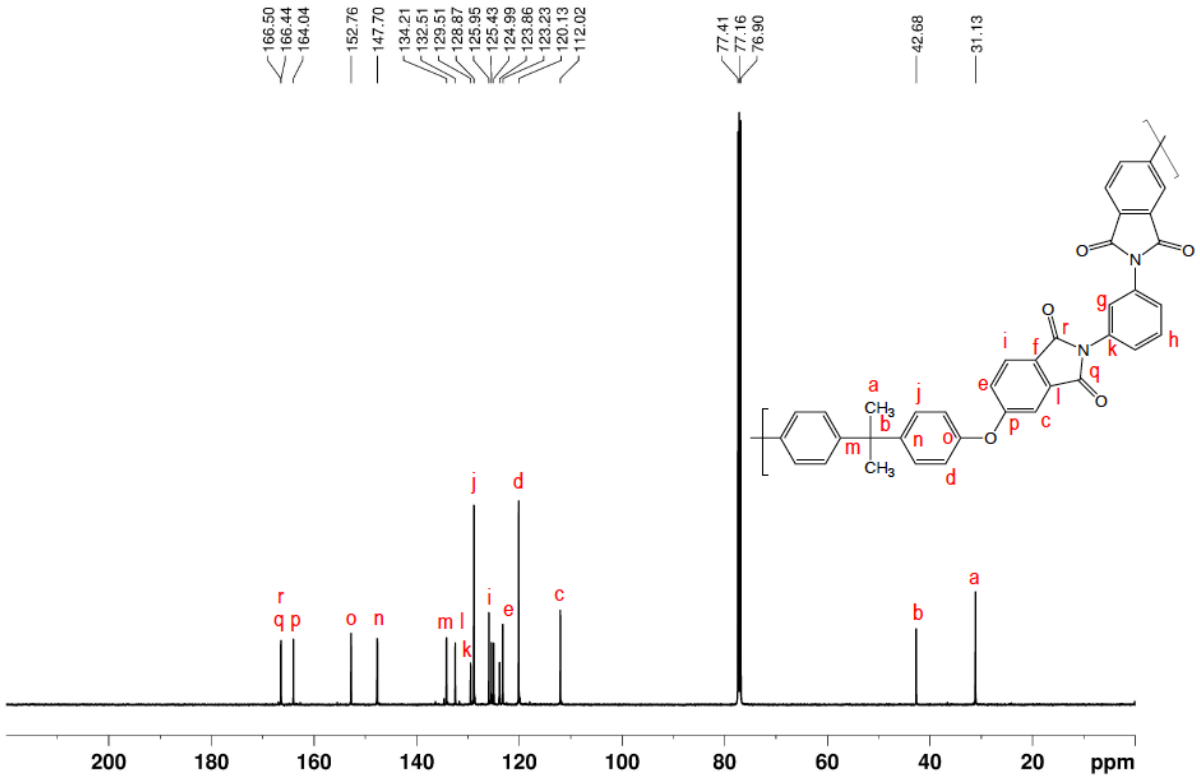


Figure S9. Dope solution rheology. a, Dynamic viscosity of a mixture of 4:1 thymol/raspberry ketone. b-f Storage (blue, solid line) and loss (green, dashed line) moduli. Ultem® solutions in different solvents: **b**, 16 wt% in thymol; **c**, 16 wt% in 4:1 thymol/raspberry ketone (TR); **d**, 20 wt% in thymol; **e**, 20 wt% in thymol/raspberry ketone (TR); **f**, 20 wt% in NMP.



^{1}H NMR	H_a	H_b	H_c	H_d	H_e	H_f	H_g	H_h	H_i
δ (ppm)	1.77	7.05	7.35	7.37	7.44	7.52	7.62	7.67	7.90
Multiplicity	s	d	d	dd	d	dd	t	T	d
Couplings	$^3J_{bC}$ (ortho) = 8.7 Hz; $^3J_{dg}$ (ortho) = 8.0 Hz; $^3J_{fi}$ (ortho) = 8.3 Hz $^4J_{dh}$ (meta) = 1.8 Hz; $^4J_{ef}$ (meta) = 2.0 Hz								

Figure S10. Spectroscopic analysis of Ultem®. 600 MHz ^{1}H NMR spectrum and peaks assignments.



^{13}C NMR	C_a	C_b	C_c	C_d	C_e	C_f	C_g	C_h	C_i
δ (ppm)	31.13	42.68	112.0	120.1	123.2	123.9	125.0	125.4	126.0
^{13}C NMR	**C_j**	**C_k**	**C_l**	**C_m**	**C_n**	**C_o**	**C_p**	**C_q**	**C_r**
δ (ppm)	128.9	129.5	132.5	134.2	147.7	152.8	164.0	166.5	166.5

Figure S11. Spectroscopic analysis of Ultem®. 600 MHz ^{13}C NMR spectrum and peak assignments.

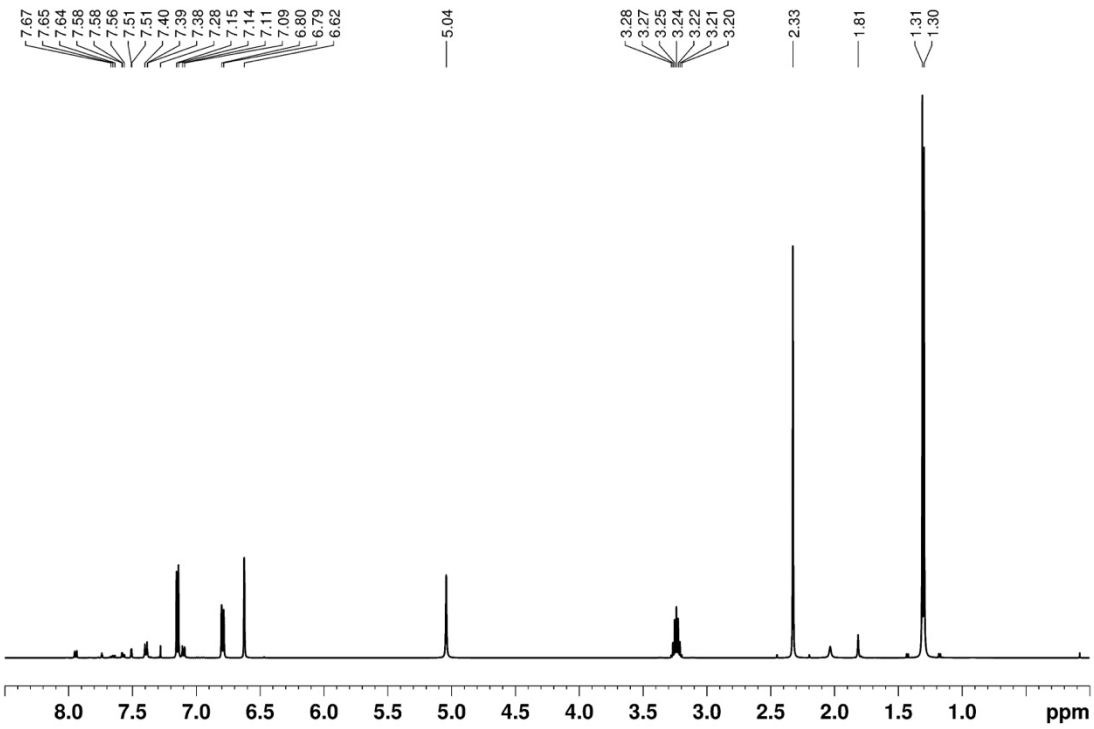


Figure S12. Spectroscopic analysis of 20 wt% Ultem® solution in thymol. 600 MHz ^{1}H NMR spectrum.

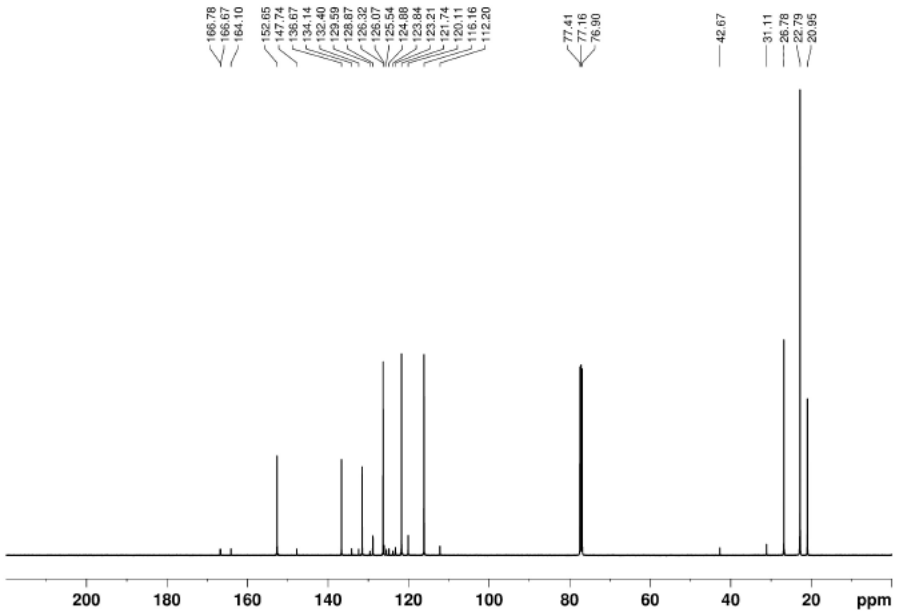


Figure S13. Spectroscopic analysis of 20 wt% of Ultem® solution in thymol. 600 MHz ^{13}C NMR spectrum.

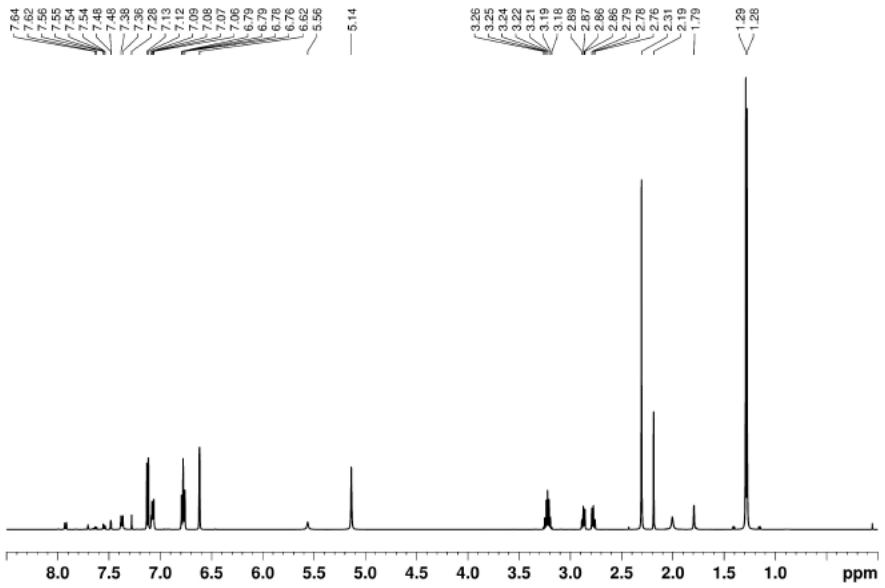


Figure S14. Spectroscopic analysis of 20 wt% of Ultem® solution in 4:1 thymol/raspberry ketone. 600 MHz ^{1}H NMR spectrum.

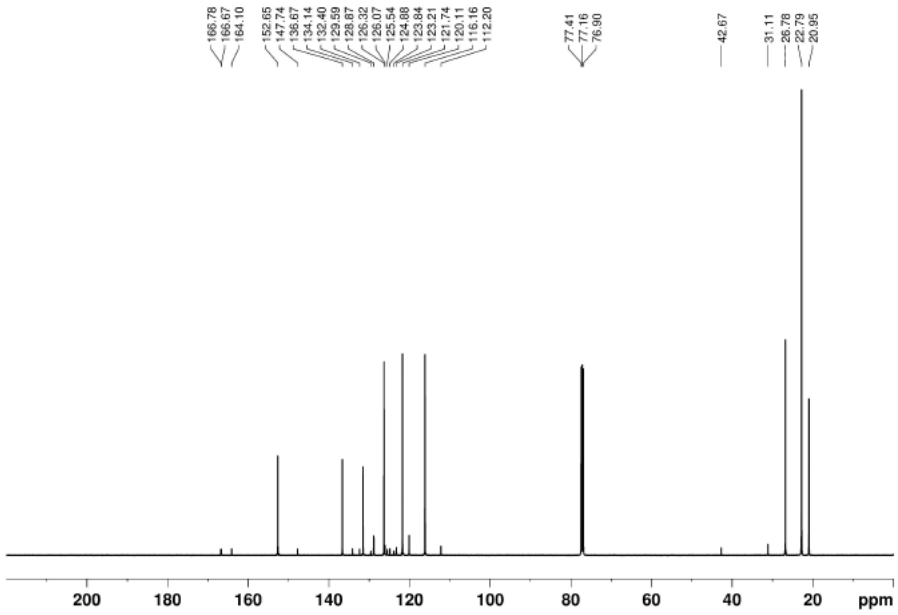


Figure S15. Spectroscopic analysis of 20 wt% of Ultem® solution in 4:1 thymol/raspberry ketone. 600 MHz ^{13}C NMR spectrum.

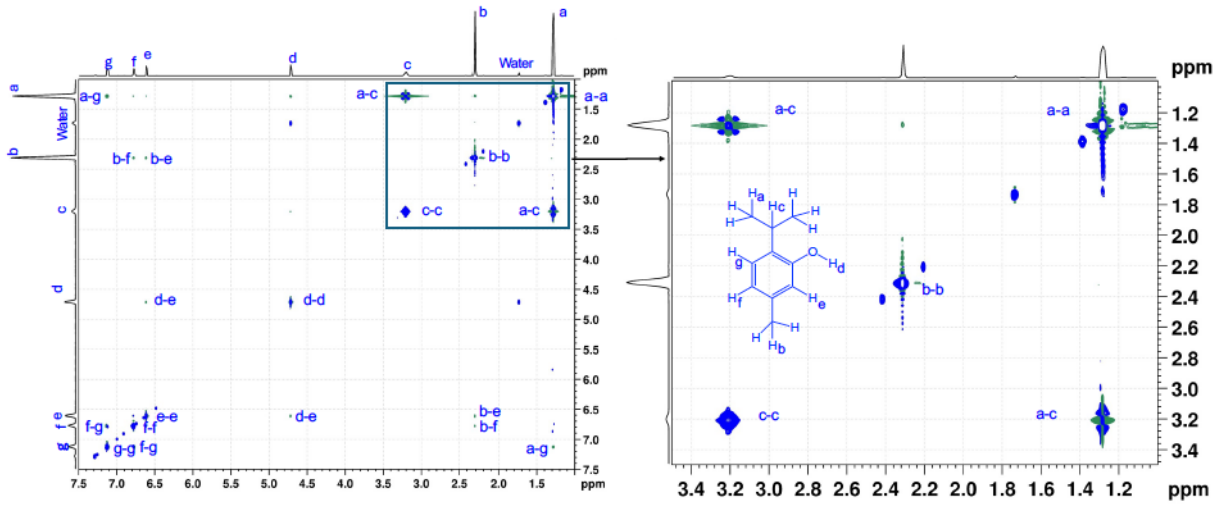


Figure S16. NOESY spectroscopic analysis of thymol. 2D ^{1}H NMR NOESY spectrum.

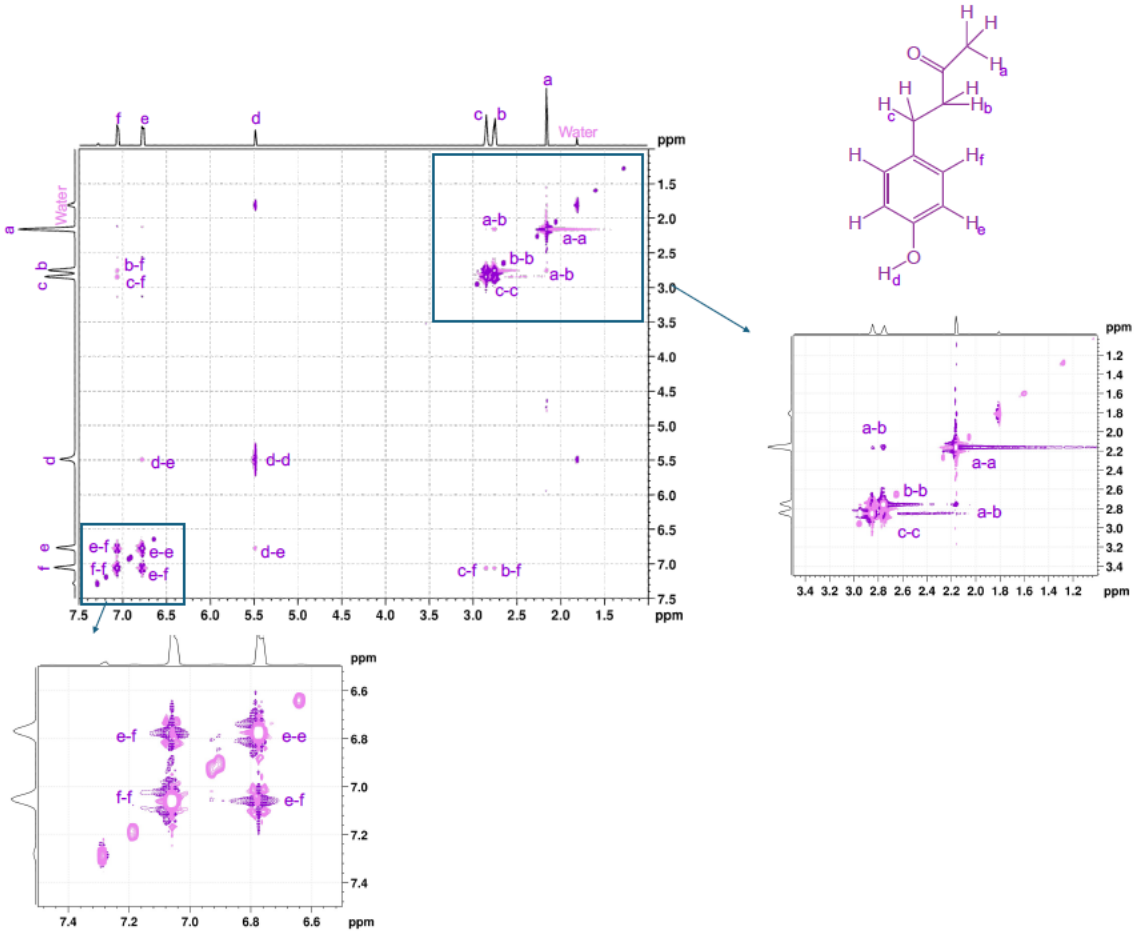


Figure S17. NOESY spectroscopic analysis of raspberry ketone. 2D ^{1}H NMR NOESY spectrum.

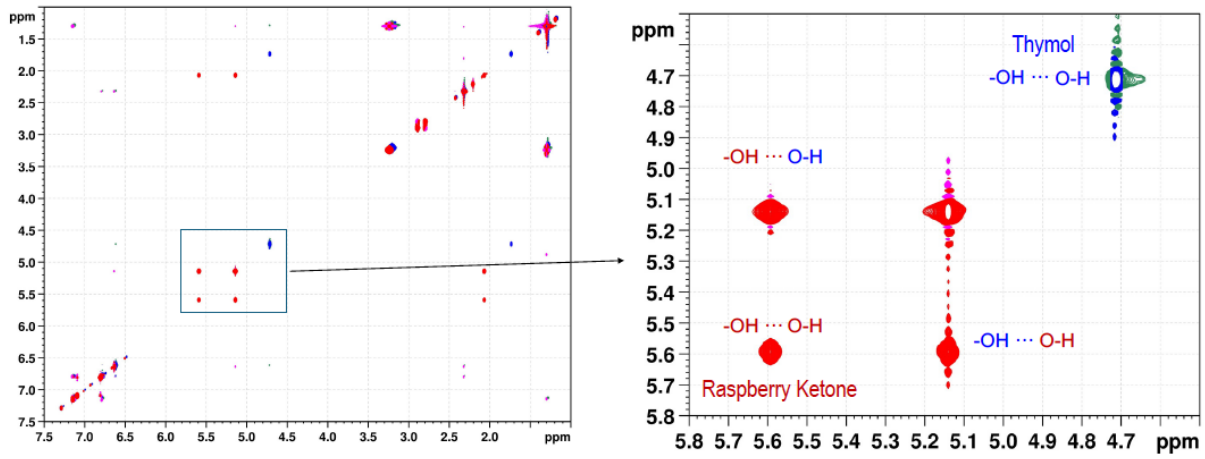


Figure S18. NOESY Spectroscopic analysis of 4:1 thymol/raspberry ketone. 2D ^{1}H NMR NOESY spectrum.

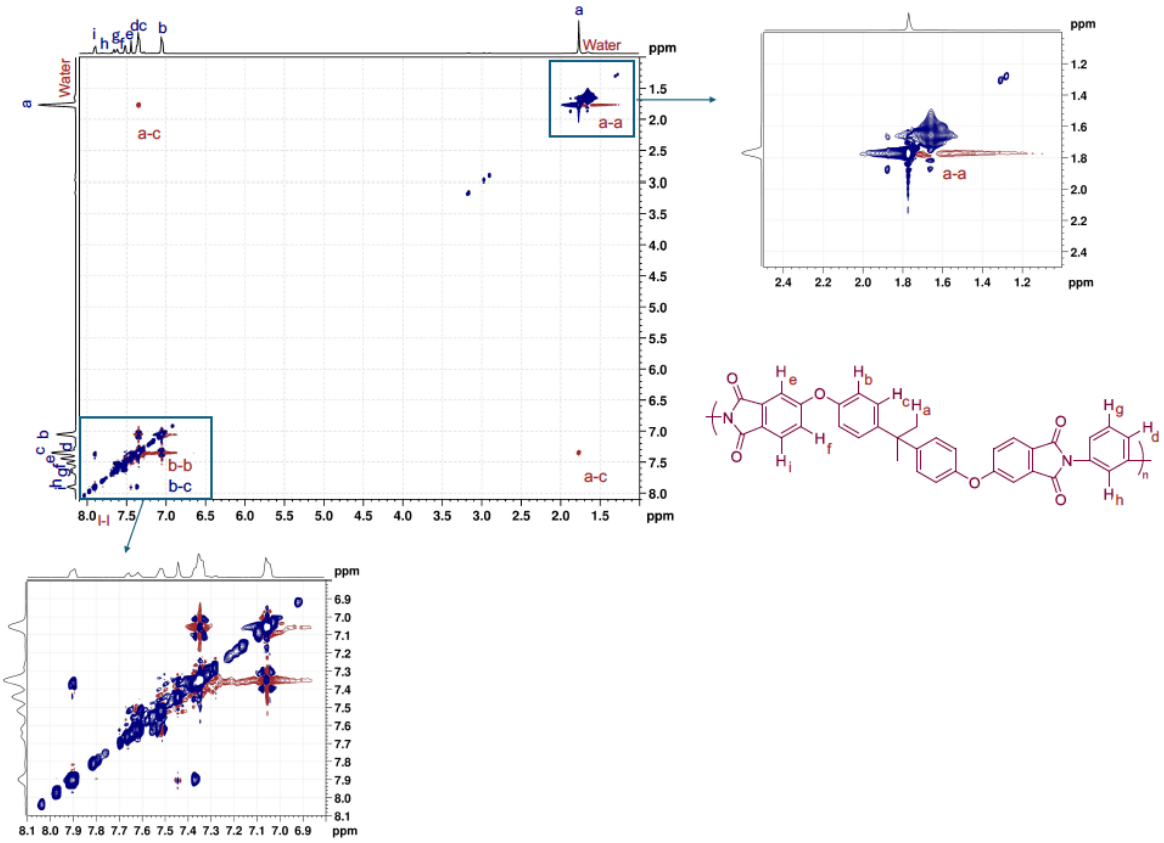


Figure S19. NOESY Spectroscopic analysis of Ultem®. 2D ^{1}H NMR NOESY spectrum.

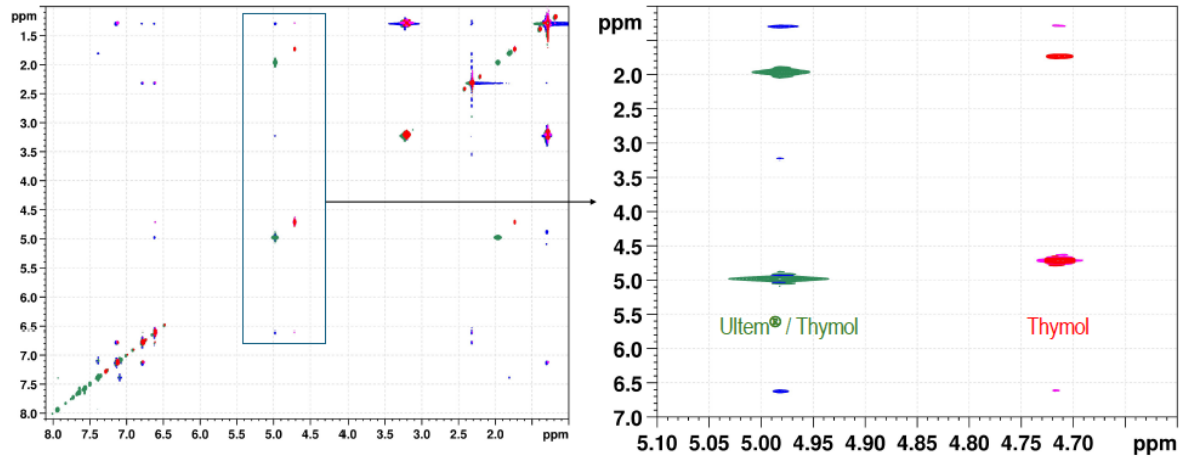


Figure S20. NOESY Spectroscopic analysis. The 2D ^{1}H NMR NOESY spectrum of Ultem® and thymol.

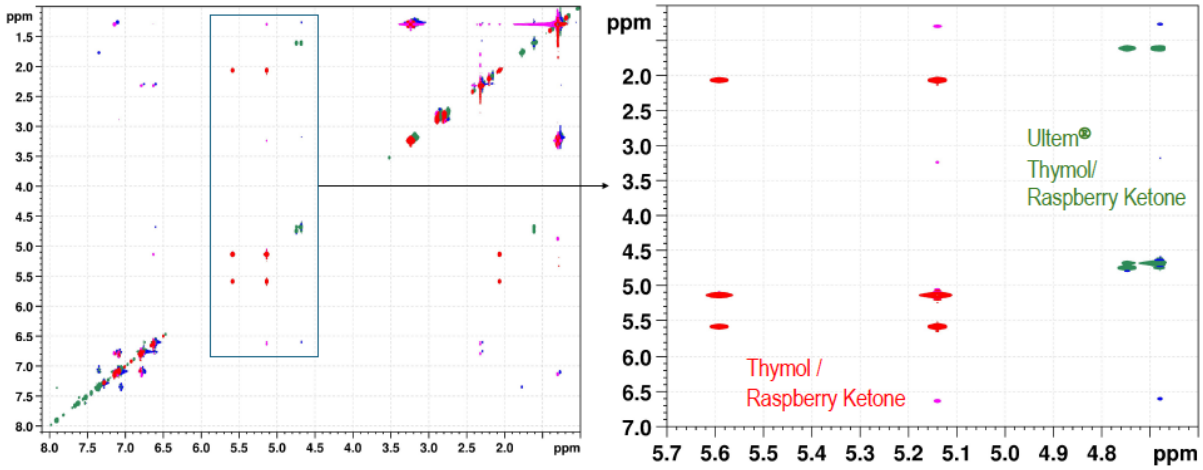


Figure S21. NOESY Spectroscopic analysis of Ultem® solution in 4:1 thymol/ raspberry ketone. 2D ^{1}H NMR NOESY spectrum.

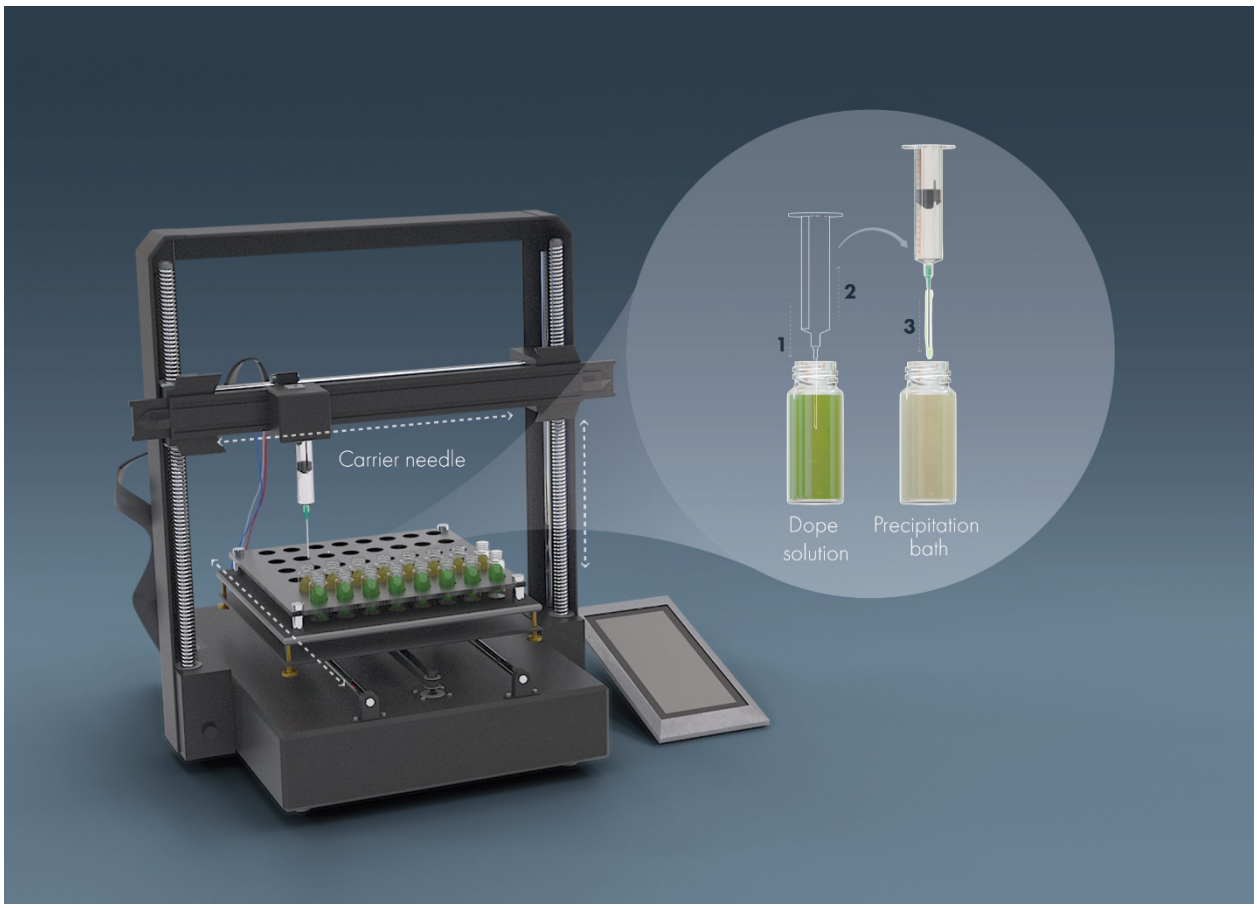


Figure S22. Automated manipulator. Schematic representation of high throughput hollow fibre fabrication.

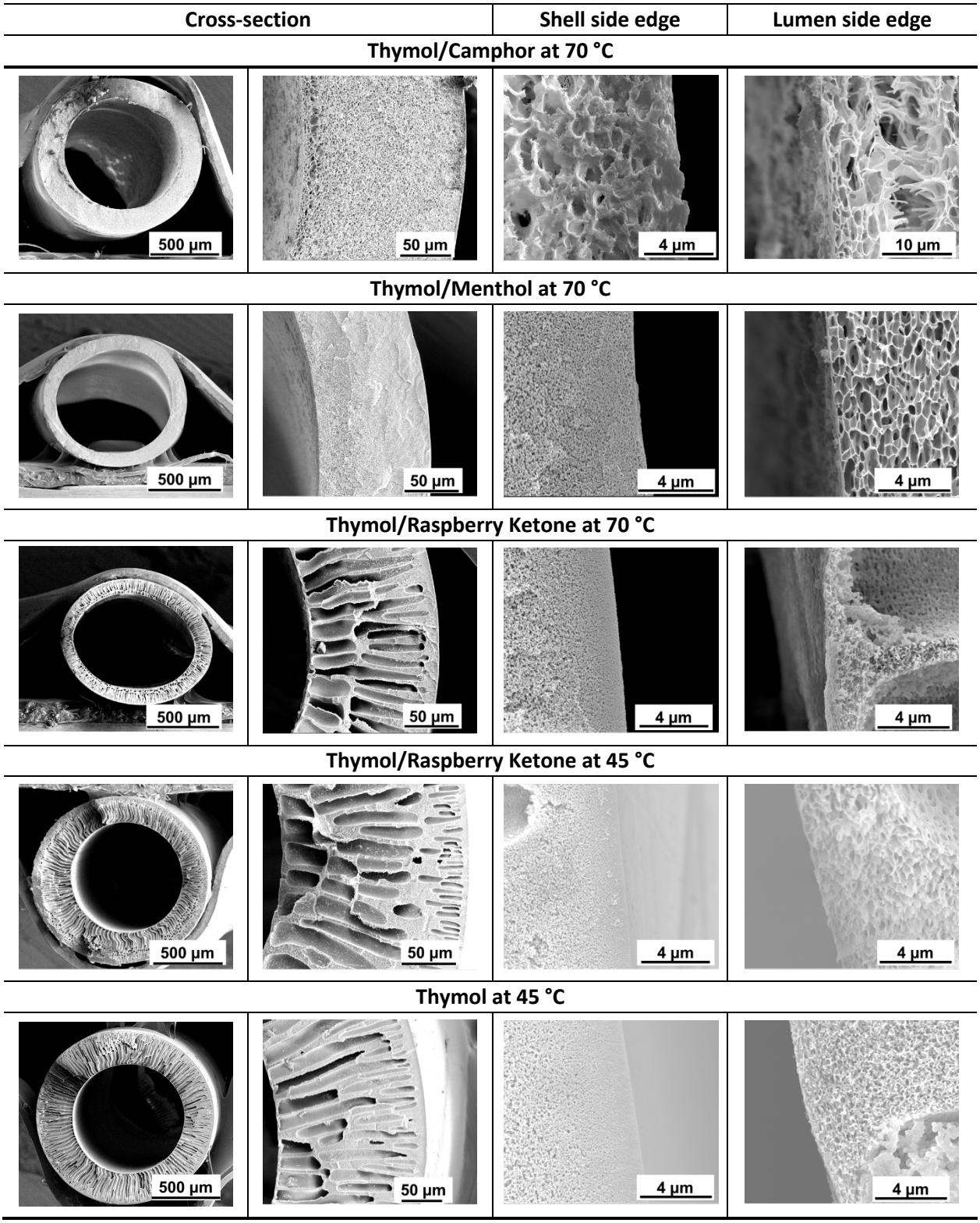


Figure S23. SEM images of hollow fibres. Hollow fibres fabricated by the automated manipulator unit using 13 wt% Ultem® dope solutions in thymol or 4:1 molar mixtures of thymol and a second natural component. Coagulation in 100% ethanol.

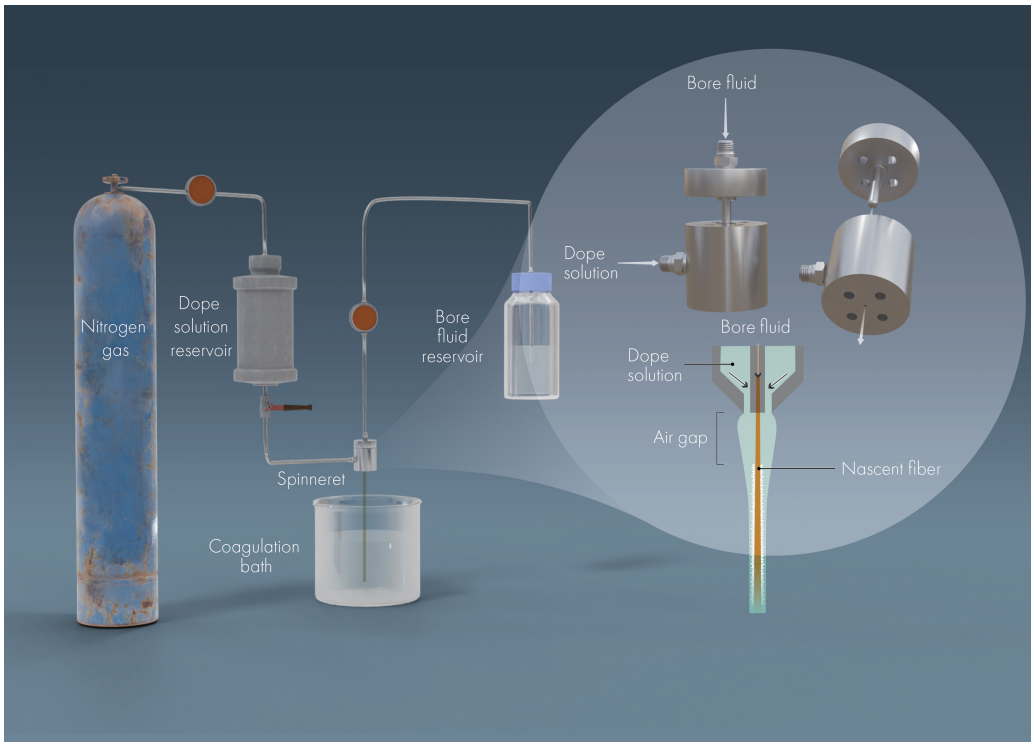


Figure S24. Schematic representation of hollow fibre fabrication by dry-jet wet spinning unit.

Table S5. Conditions for Ultem® hollow fibre spinning.

Solvent	**Thymol**		**Thymol/Raspberry Ketone**		**NMP**
Dope Ultem® conc. (wt%)	16	20	16	20	20
Dope solution temperature (°C)	45	45	45	45	25
Dope solution pressure (bar)	1.5	3.3	1,5	3.3	1.2
Air gap (cm)	1; 3; 8	3	1; 3; 8	3	3
External coagulant	Ethanol 1:1 Ethanol/Water		Ethanol 1:1 Ethanol/Water		Water
Bore fluid	Ethanol		Ethanol		Water
Bore fluid flow rate ($mL\ min^{-1}$)	0.6; 1.5; 3; 6	3; 6	0.6; 1.5; 3; 6	3; 6	6
Bore fluid temperature (°C)	22	22	22	22	22

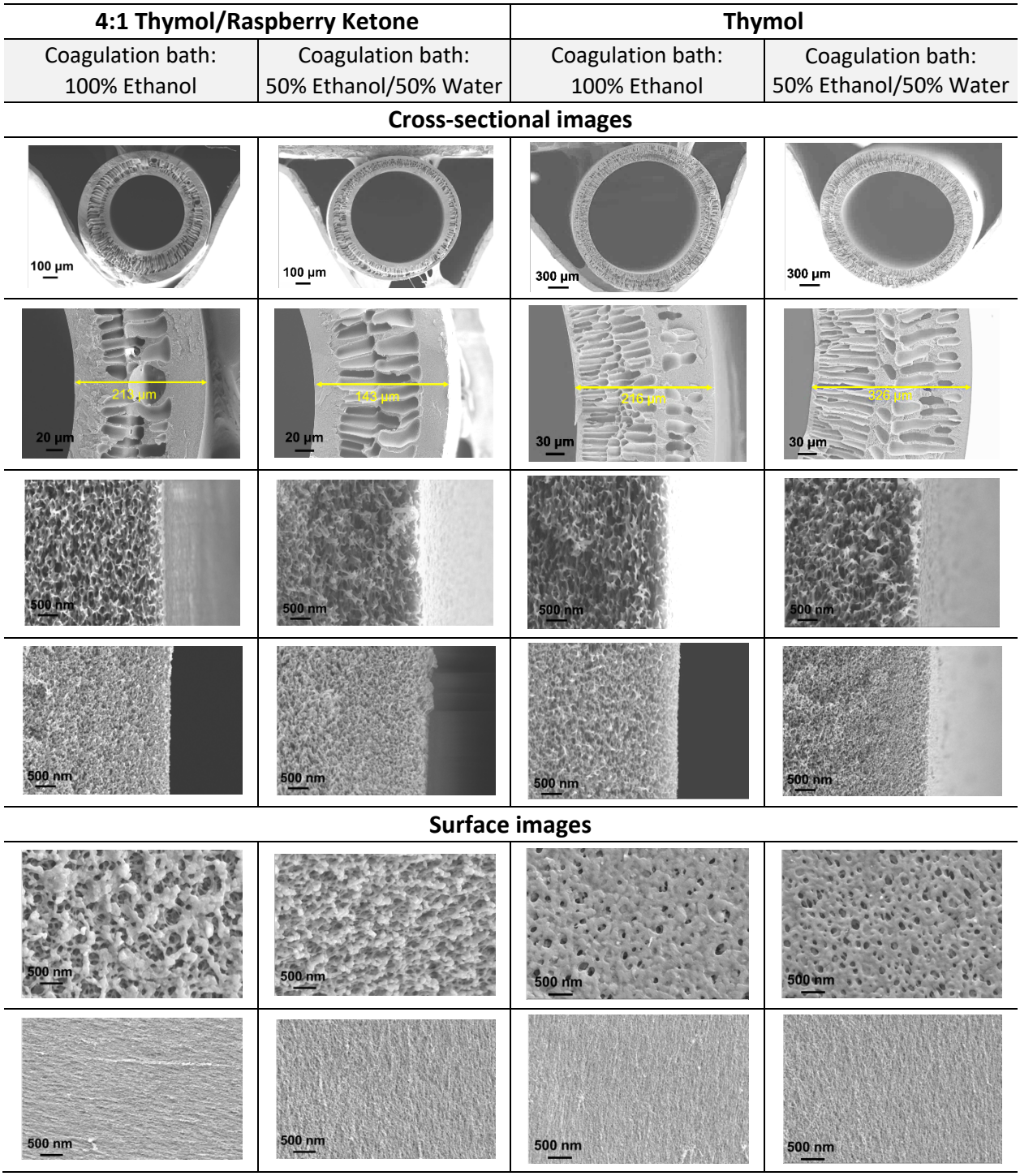


Figure S25. SEM images of hollow fibres. Hollow fibres fabricated by dry-jet wet spinning using16 wt% Ultem® dope solutions in thymol or 4:1 thymol/raspberry ketone. Bore fluid flow rate of 3 mL min^{-1} and air gap of 3 cm.

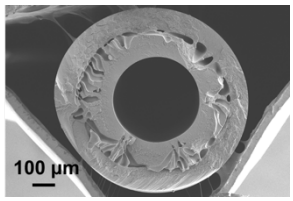
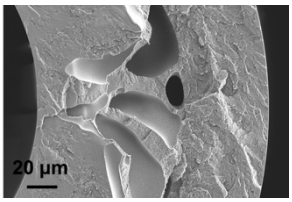
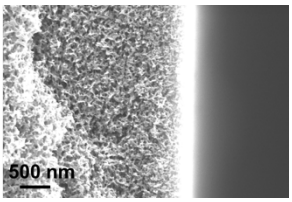
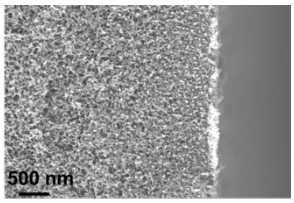
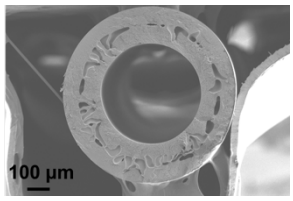
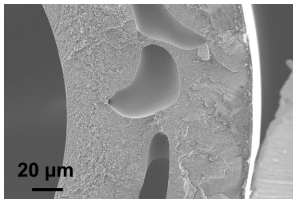
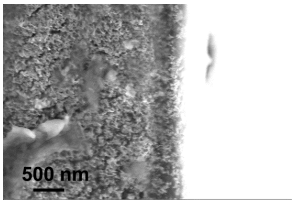
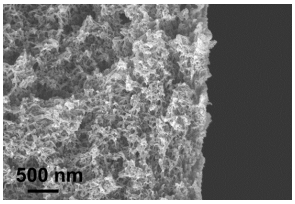
Cross-section		Shell side edge	Lumen side edge
4:1 Thymol/Raspberry Ketone			
			
Thymol			
			

Figure S26. SEM images of hollow fibres. Hollow fibres fabricated by dry-jet wet spinning using 20 wt% Ultem® dope solution in thymol or 4:1 thymol/raspberry. Bore fluid flow rate of 6 mL min^{-1} and air gap of 3 cm. Coagulation bath: 100% ethanol.

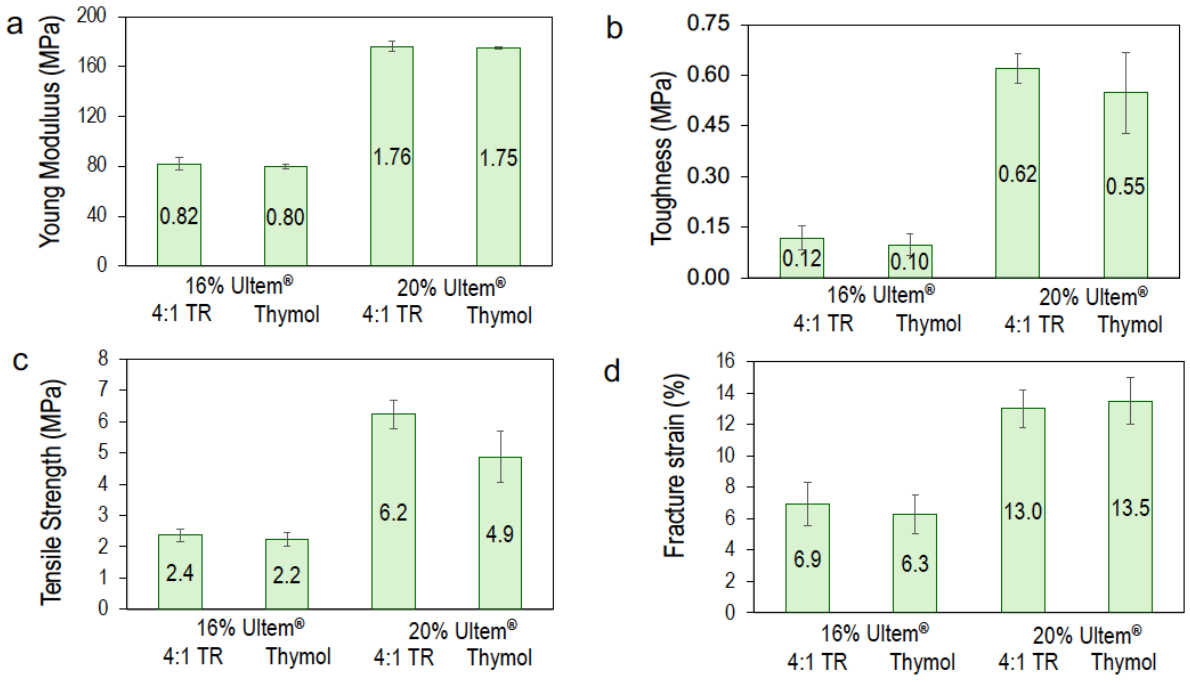


Figure S27. Mechanical properties. Hollow fibres fabricated in a continuous spinning machine by using Ultem® dope solutions in thymol and 4:1 thymol/raspberry ketone.

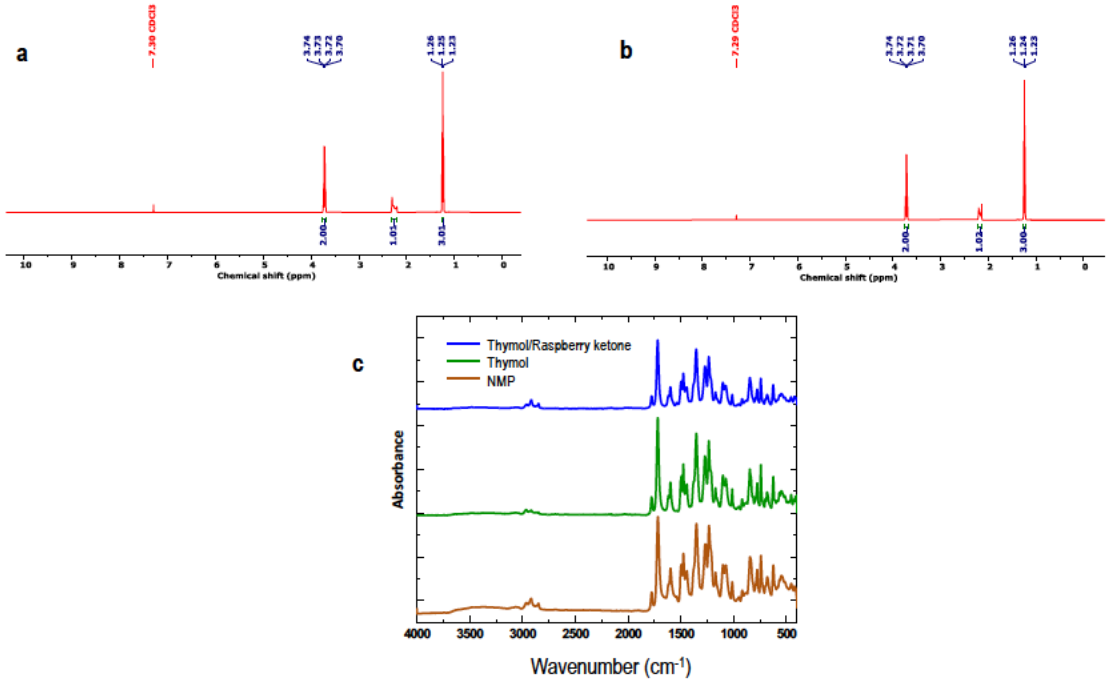


Figure S28. Spectroscopic confirmation that thymol was not presence after the hollow fibers preparation. ^{1}H NMR spectrum of **a**, pure ethanol and **b**, (2.58 g) ethanol exposed to (0.0129 g) hollow fibers for 72 h. c, FTIR spectrum of fibers fabricated from dope solutions in different solvents (4:1 thymol/raspberry ketone, thymol and NMP).

Table S6. Water vapour permeability and selectivity (H_2O/N_2) of hollow fibres prepared with 16 wt% Ultem® dope solution in thymol or 4:1 thymol/raspberry ketone, coagulated in 50% ethanol / 50% water, and coated with tannic acid (TA), sodium periodate ($NAIO_4$) and hyperbranched polyethyleneimine (PEI).

Coating type	Water vapor permeance (GPU)	H_2O/N_2 Selectivity	Mode	Temperature (°C)
4:1 Thymol/Raspberry Ketone				
No Coating	16,453	12.3	Vacuum	25.0
TA-10, $NaIO_4$-10 min	11,001	658	Vacuum	25.0
TA-10, $NaIO_4$- 10, PEI 15 min	6,134	53,453	Vacuum	25.0
TA-10, $NaIO_4$-10, PEI 15 min	4,566	44,654	Sweep	25.0
TA-10, $NaIO_4$-10, PEI 15 min	5,678	49,365	Vacuum	32.5
TA-10, $NaIO_4$-10, PEI 15 min	4,056	42,453	Sweep	32.5
TA-10, $NaIO_4$-10, PEI 15 min	5,453	45,611	Vacuum	35.0
Thymol				
No Coating	28,633	11.5	Vacuum	25.0
TA-10, $NaIO_4$-10 min	12,385	555	Vacuum	25.0
TA-10, $NaIO_4$-10, PEI 15 min	6,689	49,385	Vacuum	25.0
TA-10, $NaIO_4$-10, PEI 15 min	4,989	42,441	Sweep	25.0
TA-10, $NaIO_4$-10, PEI 15 min	6,034	48,108	Vacuum	32.5
TA-10, $NaIO_4$-10, PEI 15 min	4,554	40,005	Sweep	32.5
TA-10, $NaIO_4$-10, PEI 15 min	5,766	44,339	Vacuum	35.0