

Supplementary Materials of the paper:

Polymorphism of Spirolactone: an unprecedented case of monotropy turning to enantiotropy with a huge difference in the melting temperatures

by

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Heat capacity (C_p) of form II and for the supercooled liquid of Spirolactone

Form II [data fitting range: 250 – 450 K]

$$C_p (\text{J g}^{-1} \text{K}^{-1}) = (0.2148 \pm 0.0043) - (0.001502 \pm 0.000025) \cdot T(\text{K}) + (4.186 \pm 0.036) \cdot 10^{-6} \cdot T^2(\text{K}) \quad (\text{S.1})$$

$$R^2 = 0.9990$$

Liquid [data fitting range: 325 -450 K]

$$C_p (\text{J g}^{-1} \text{K}^{-1}) = (0.2706 \pm 0.0093) + (0.000468 \pm 0.000024) \cdot T(\text{K}) \quad (\text{S.2})$$

$$R^2 = 0.94$$

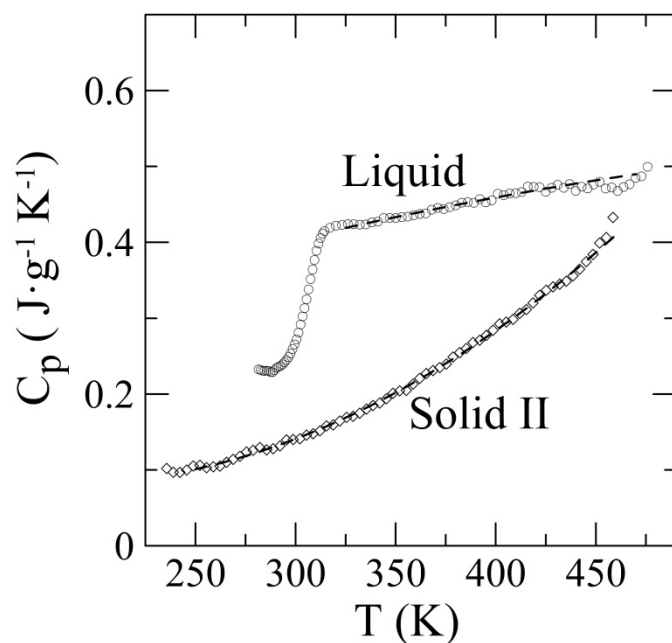


Figure S.1. C_p as a function of the temperature of the undercooled liquid phase and of form II. The dashed lines are the fits provided above.

Table S.1. Selected C_p values

SOLID II		LIQUID	
T/K	C_p Experimental J/gK	T/K	C_p Experimental J/gK
250	0.1063	325	0.4240
255	0.1034	330	0.4236
260	0.1067	335	0.4236
265	0.1092	340	0.4275
270	0.1144	345	0.4312
275	0.1205	350	0.4321
280	0.1272	355	0.4331
285	0.1260	360	0.4369
290	0.1292	365	0.4382
295	0.1388	370	0.4460
300	0.1409	375	0.4552
305	0.1406	380	0.4488
310	0.1515	385	0.4514
315	0.1572	390	0.4548
320	0.1610	395	0.4527
325	0.1692	400	0.4624
330	0.1723	405	0.4617
335	0.1801	410	0.4648
340	0.1861	415	0.4746
345	0.1933	420	0.4736
350	0.2031	425	0.4667
355	0.2044	430	0.4742
360	0.2148	435	0.4740
365	0.2258	440	0.4681
370	0.2321	445	0.4692
375	0.2391	450	0.4793
380	0.2511		
385	0.2598		
390	0.2701		
395	0.2773		
400	0.2900		
405	0.2942		
410	0.3050		
415	0.3118		
420	0.3180		
425	0.3364		
430	0.3407		
435	0.3488		
440	0.3608		
445	0.3745		
450	0.3831		

Heat of fusion of form II at the melting point of form I

Kirchhoff:

$$\Delta_{II \rightarrow L} H(T_{I \rightarrow L}) = \Delta_{II \rightarrow L} H(T_{II \rightarrow L}) + \int_{T_{II \rightarrow L}}^{T_{I \rightarrow L}} \Delta_{II \rightarrow L} C_p dT \quad \text{S.3}$$

$$\text{with } \int_{T_{II \rightarrow L}}^{T_{I \rightarrow L}} \Delta_{II \rightarrow L} C_p dT = \int_{T_{II \rightarrow L}}^{T_{I \rightarrow L}} (C_{p,L} - C_{p,II}) dT \quad \text{S.4}$$

$\Delta_{II \rightarrow L} C_p$ is obtained by subtracting eq. S.1 from eq. S.2 and hence

$$\Delta_{II \rightarrow L} C_p = 0.0558 + 0.00197 T - 4.186 \times 10^{-6} T^2 \quad \text{S.5}$$

Integrating the right-hand side of S.5 one obtains

$$\Delta_{II \rightarrow L} C_p dT = 0.0558 T + 0.000985 T^2 - 1.395 \times 10^{-6} T^3 \quad \text{S.6}$$

With the two integration limits $T_{II \rightarrow L} = 479.6$ K and $T_{I \rightarrow L} = 408$ K and $\Delta H_{II \rightarrow L}(T_{II \rightarrow L}) = 54.0$ J g⁻¹, one obtains for S.3:

$$\Delta H_{II \rightarrow L}(T_{I \rightarrow L}) = 54.0 \text{ J g}^{-1} - 7.458 \text{ J g}^{-1} = 46.5 \text{ J g}^{-1} \quad \text{S.7}$$

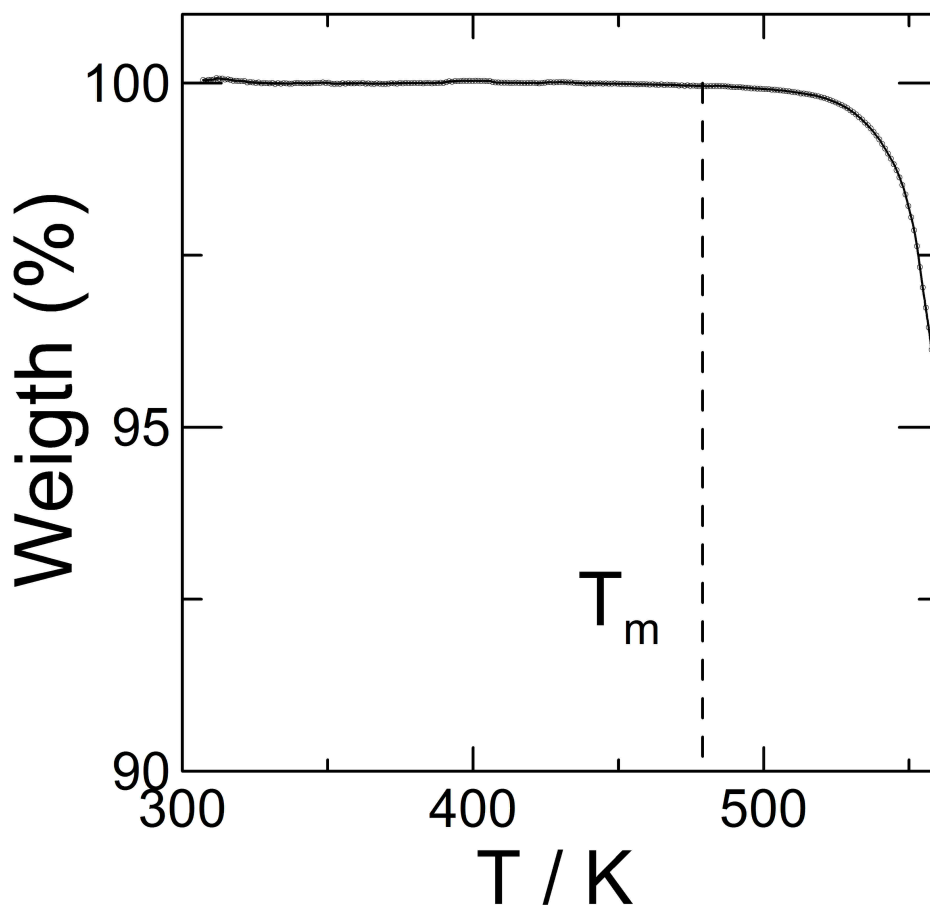


Figure S2. Thermogravimetric data of form I obtained by recrystallization of the Sanofi batch from ethanol. No trace of residual solvent is observed.