

Supporting Information:

**Relation between the intermolecular interactions of  
Carbonyl (PC) with Nitrile (HNBR) functional groups  
and the Flash point of a gel polymer electrolyte.**

*Caroline St-Antoine,<sup>a</sup> David Lepage,<sup>a</sup> Gabrielle Foran,<sup>a</sup> Arnaud Prébé,<sup>a</sup> David Aymé-Perrot,<sup>b</sup>  
Dominic Rochefort<sup>a</sup> and Mickaël Dollé<sup>\*a</sup>*

<sup>a</sup> Department of Chemistry, Université de Montréal; Campus MIL, 1375 Thérèse-Lavoie-Roux  
Avenue, Montreal, Quebec, Canada, H2V 0B3

<sup>b</sup> TotalEnergies SE, 2 Pl. Jean Millier, La Défense 6, 92 078, Paris (France)

**Author information**

Corresponding author: Mickaël Dollé \*

E-mail : mickael.dolle@umontreal.ca

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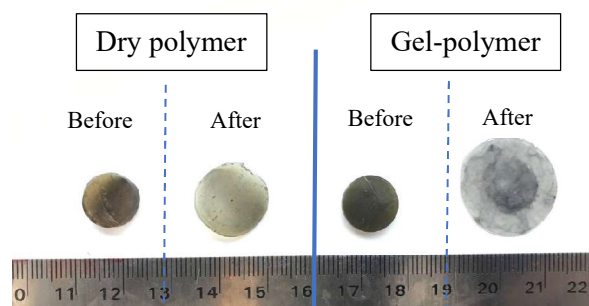
### S1 Mechanical test of HBBR with and without 20 wt% PC

Table S1 displays the results of a mechanical deformation test for the polymer 17% ACN+ 24.5 wt% LiTFSI with and without added propylene carbonate. All HNBR have similar mechanical properties regardless of ACN content; and therefore, only one example is presented here. The initial thickness of the polymers or the gel polymers were  $(1.6 \pm 0.15)$  mm with a diameter of around 12 mm. Samples were placed in the oven at a temperature of 80 °C under a weight of 2 lb (pressure of 11 Psi). After 1 h, the samples were cooled down, and the new thickness and diameter were measured to evaluate the permanent deformation of the sample.

Sample	Initial thickness (mm)	Initial diameter (mm)	Final thickness (mm)	Final diameter (mm)	thickness remained (%)	Diameter gained (%)	Average thickness left (%)	Average Increase diameter (%)
17% ACN + 24.5 wt% LiTFSI	1.48	12.0	1.15	14.0	77.73	116.7	76.11	116.7
	1.43	12.0	1.14	14.0	79.89	116.7		
	1.42	12.0	1.15	14.0	81.27	116.7		
	1.73	10.7	0.72	17.0	41.32	158.9		
17% ACN + 24.5% LiTFSI + 20 wt% PC	1.74	11.0	0.79	17.3	45.74	157.3	35.73	166.5
	1.62	12.0	0.65	22.0	20.12	183.3		

**Table S1.** table 1 shows the permanent deformation with the percentage of thickness remaining and the percentage diameter gained after being compress by a 2 lbs weight at 80 °C for 1 h.

Figure S1 illustrates the dry and the gel polymer before and after the treatment.



**Figure S1.** Picture of the dry polymer electrolyte 17% ACN + LiTFSI and the gel polymer electrolyte 17% ACN + LiTFSI + 20 wt% PC before and after being heated at 80 °C under a pressure of 11 Psi.

The line between a plasticized polymer and a gel-polymer electrolyte is not well defined. The objective of S1 is to demonstrate that our gel-polymer maintains some of the mechanical properties of the neat polymer. Although mechanical strength decreases as PC is added to the polymer, the gel-polymer remains solid and is still resistant to deformation to some extent.

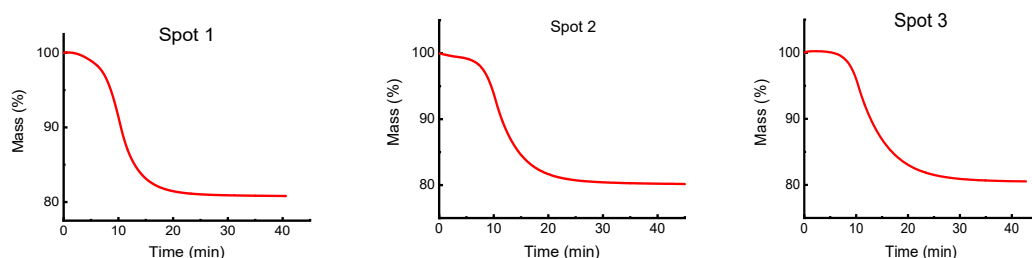
**S2 Optical photography of the gel-polymer**



**Figure S2.** Optical picture of the polymer HNBR 35% ACN doped with 20 wt% PC.

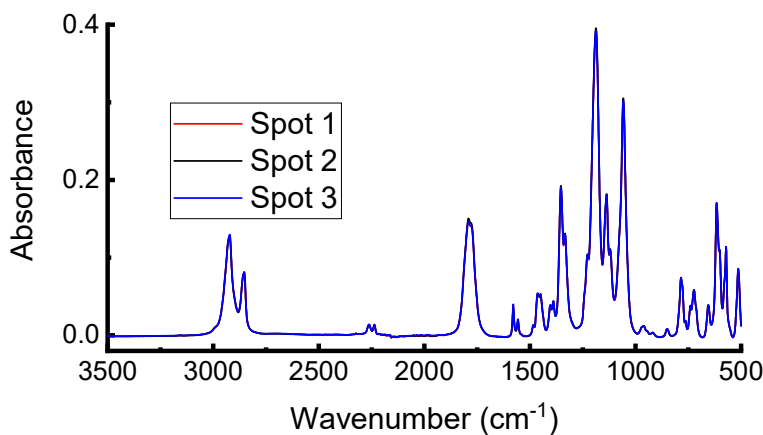
### S3 TGA and FT-IR to verify sample preparation technique.

HNBR does not readily absorb PC, especially when LiTFSI is added to the mixture. In previous tests, some free PC was observed on the polymer surface. By heating the sample as described in the experimental section, a homogeneous gel-polymer phase was obtained without any loss of solvent. TGA measurements had been done at different spots on the polymer to verify that 20 wt% solvent was uniformly distributed in the polymer and to verify that the solvent did not evaporate during the heating process. Also, FT-IR (ATR mode) had been done on different spots, and for both sides of the 800  $\mu\text{m}$  polymers to verify that the solvent completely penetrated the polymer to create a homogeneous gel polymer. Examples of TGA and FT-IR spectra for the gel-polymer 36% ACN + PC + LiTFSI are shown below. Figure S3a demonstrates 3 TGA measurements done on three different spots of the gel-polymer 36% ACN + PC + LiTFSI.



**Figure S3a.** TGA (35 °C to 242 °C at 20 °C/min and isothermal at 242 °C for 50 min) done at three different spots on the gel-polymer 36% ACN + PC + LiTFSI demonstrating that 20 wt% PC was uniformly applied to the gel polymer.

Figure S3b shows the FT-IR spectrum at different places on the gel-polymer electrolyte 36% ACN + PC + LiTFSI. The three spectra were taken in ATR mode with the FT-IR PerkinElmer Spectrum two at a resolution of 4  $\text{cm}^{-1}$ .

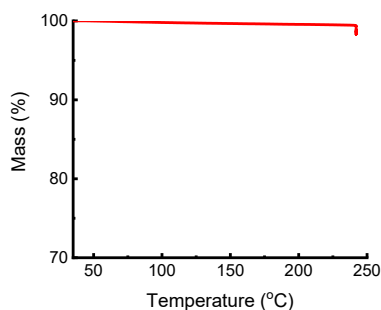


**Figure S3b.** FT-IR spectra of different spots of the gel-polymer 36% ACN + PC + LiTFSI. The sample is so homogenous that the three spectra are almost identical. Because the spectra are superimposed, only the blue spectra can be seen in the figure.

The TGA shows a loss of mass of  $(20 \pm 2)\%$  for the three different spots of the analyzed sample. Also, the FT-IR spectra are similar on the three different places of the gel-polymer electrolyte. These results confirm that the presented preparation technique yields gel polymers that are homogeneous and contain 20 wt% PC.

#### S4 TGA of the polymer without solvent.

TGA analysis of 50% ACN + LiTFSI was conducted using the same experimental method without propylene carbonate in the polymeric matrix. The objective was to demonstrate that the polymeric matrix does not contribute to the loss of mass seen in the TGA measurement. 50% ACN with LiTFSI was chosen as the example because it is the polymer that is the most likely to degrade, as the nitrile and the LiTFSI degrade at a lower temperature than the carbon chains do.

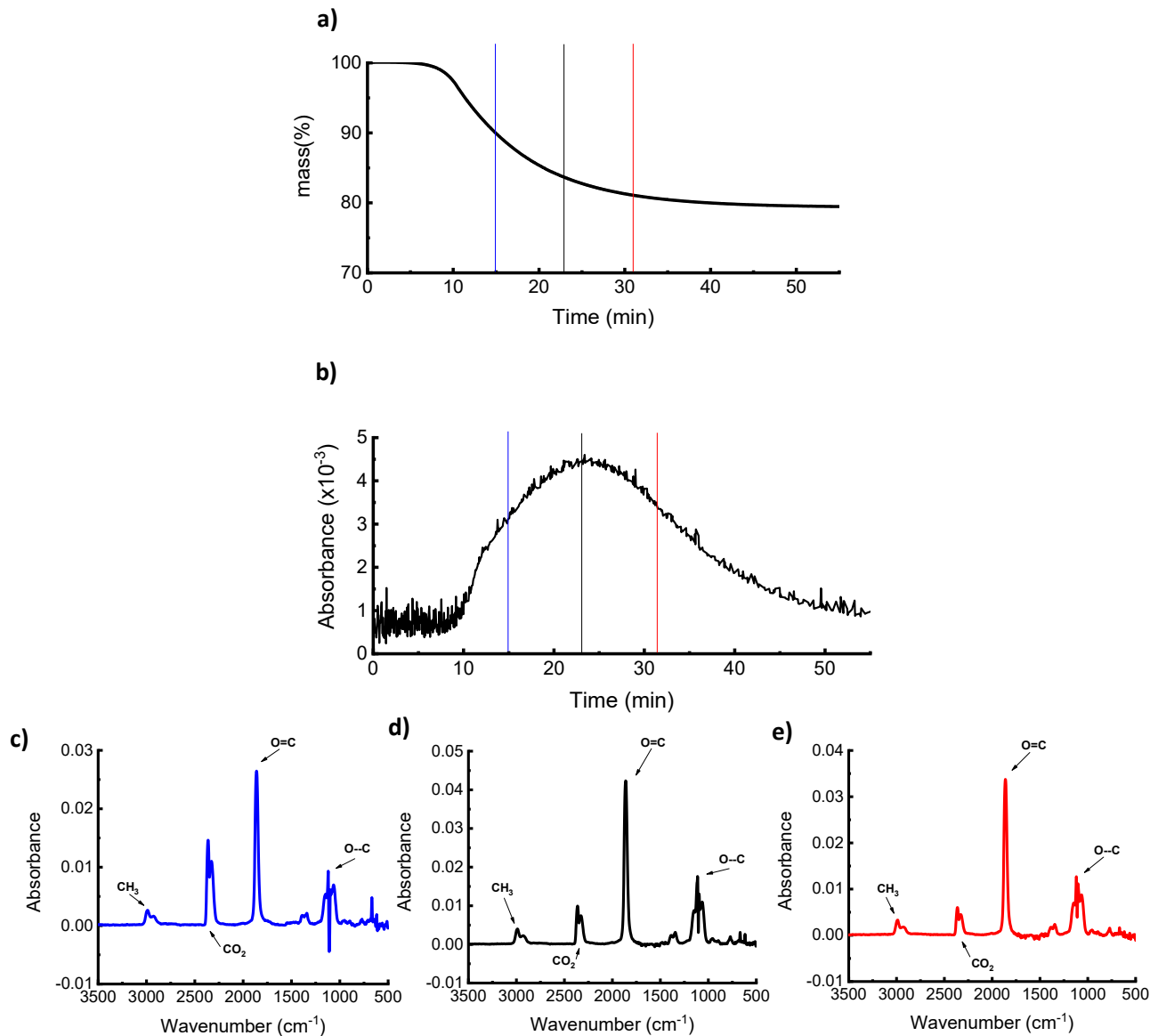


**Figure S4.** Percentage mass loss of 50% ACN with LiTFSI measured using TGA (from 35 °C to 242 °C at 20 °C/min and then isothermal at 242 °C for 50 min) vs. time.

The figure above shows that there is negligible mass loss (less than 1%) when there is no solvent trapped in the polymeric matrix. Therefore, the polymer did not contribute to the mass loss that was observed in the TGA presented in figure 4 of the article.

## S5 TGA-IR of the gel polymer 50%ACN + PC + LiTFSI

The TGA system is connected to an FT-IR spectrometer to analyze the gas evaporating as the sample is heated. PerkinElmer Spectrum two is used for the FT-IR measurement with a resolution of  $8\text{ cm}^{-1}$  and a spectral acquisition time of 2.70 seconds. Figure S8 shows FT-IR spectra at different acquisition times.



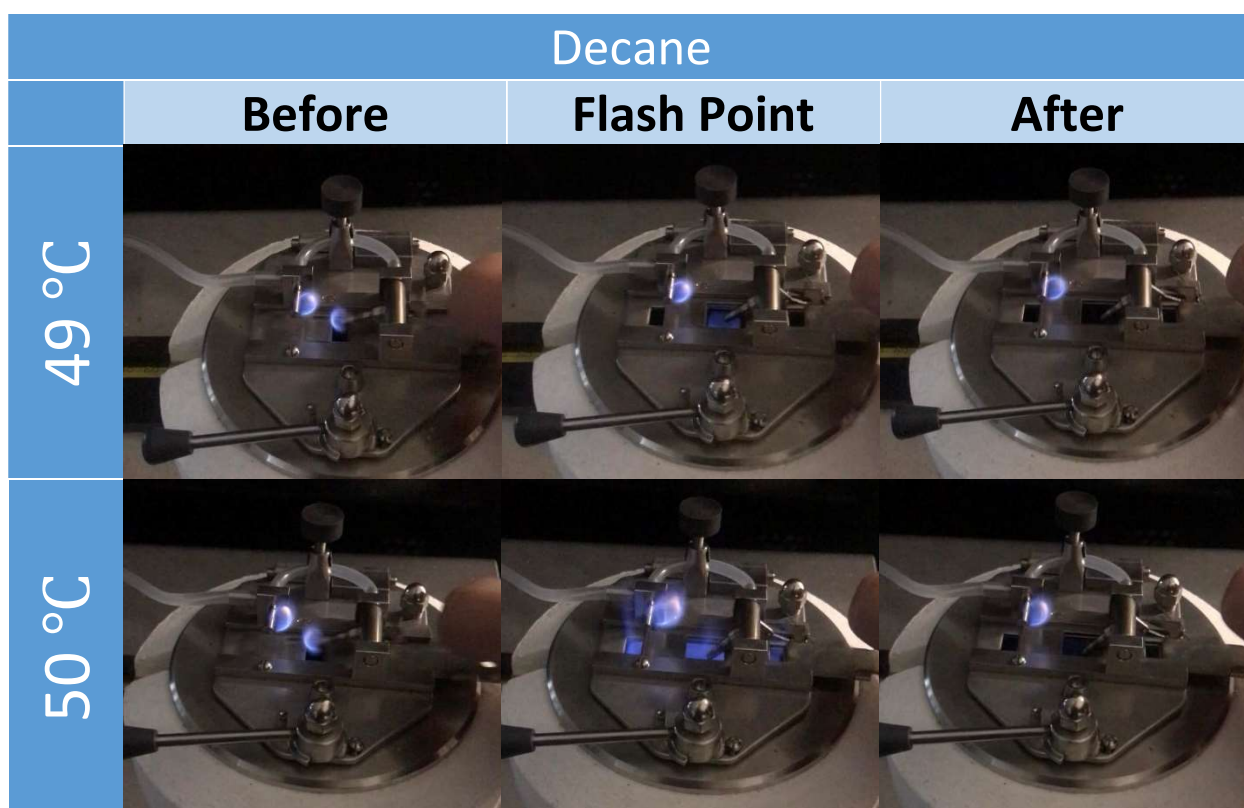
**Figure S5.** a) TGA of the sample 50% ACN + PC + LiTFSI b) Gram-Schmidt signal as a function of time c, d, e) FT-IR spectra at 15(c), 23(d) and 32(e) minutes.

The first graph (S5a) shows the mass loss as a function of time for the gel-polymer 50% ACN + PC + LiTFSI. This gel polymer was chosen as an example because the higher percentage of nitrile and LiTFSI are likely to react with PC. In figure S5b, Gram-Schmidt signals shows the sum of the entire IR absorbance for all wavenumbers as a function of the time of evaporation during TGA measurement. Three different moments were chosen: when the PC started to evaporate, at the maximum evaporation rate and at the end of the evaporation. These moments are represented by the blue, black and red lines in the TGA and RMS

spectra. The IR spectra of the gas analysis at those moments are shown in S5c, d,e. For each case, propylene carbonate is detected. The three principal carbonate peaks are: carbonyl at  $1800\text{ cm}^{-1}$ , C-O-C at  $1150\text{ cm}^{-1}$  and carbons  $\text{CH}_3$  at  $2900\text{-}3000\text{ cm}^{-1}$ . A small amount of  $\text{CO}_2$  was also detected.

### S6 Flash Point of decane in the visual light spectrum.

Figure S6 presents the flash point of the decane at  $49\text{ }^\circ\text{C}$  and  $50\text{ }^\circ\text{C}$  in the visual light spectrum. The frame was captured when the lid was opened, when the flash point is expected and after the flash point. The test was conducted with 2 ml of solvent so that the flame could be intensified and seen in the visual light spectrum. The goal was to prove that decane can be used as an accurate flash point standard. Decane was used as a standard to create a systematic method to analyze the flash point measurements. Its flash point must therefore be measured reliably.



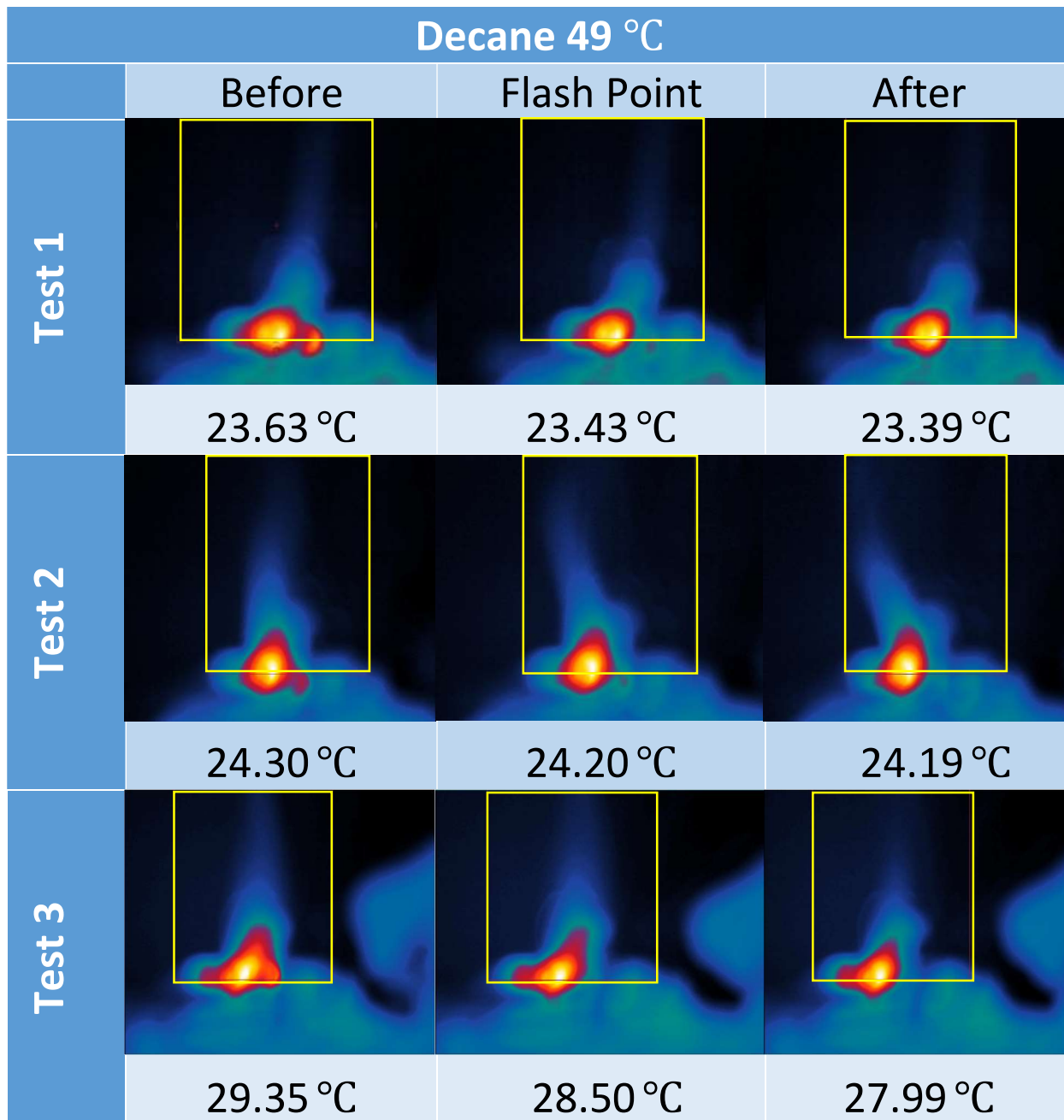
**Figure S6.** flash point measurement of 2 ml of decane in the visible light spectrum. Pictures of before and after the opening of the lid are represented.

As it can be seen in figure S6, the ignition of the decane vapor occurs at a temperature of  $50\text{ }^\circ\text{C}$  when the flame entered the chamber of the instrument. No notable ignition occurs when the same experiment is conducted at  $49\text{ }^\circ\text{C}$  which is below the flash point of decane.



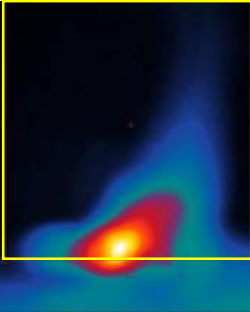
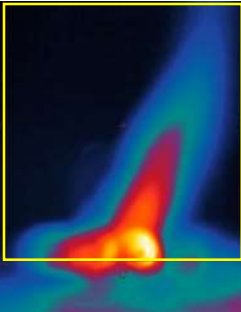
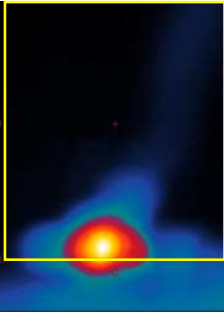
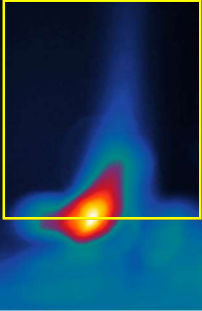
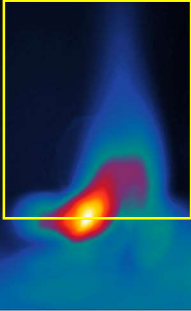
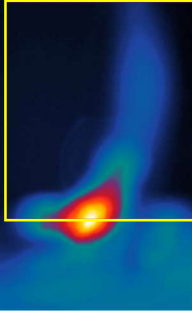
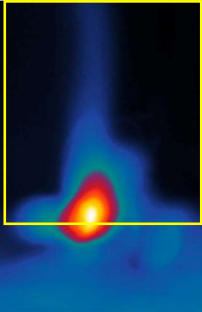
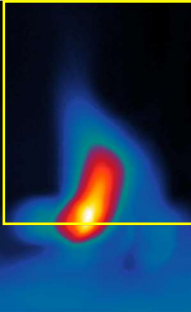
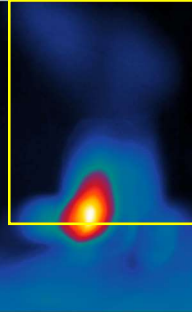
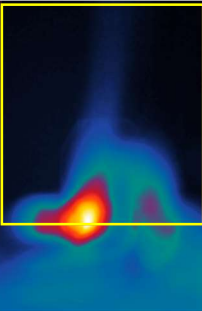
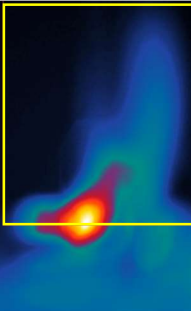
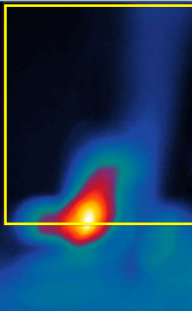
### S7 Flash point of decane at 49 °C and 50 °C in the IR spectrum

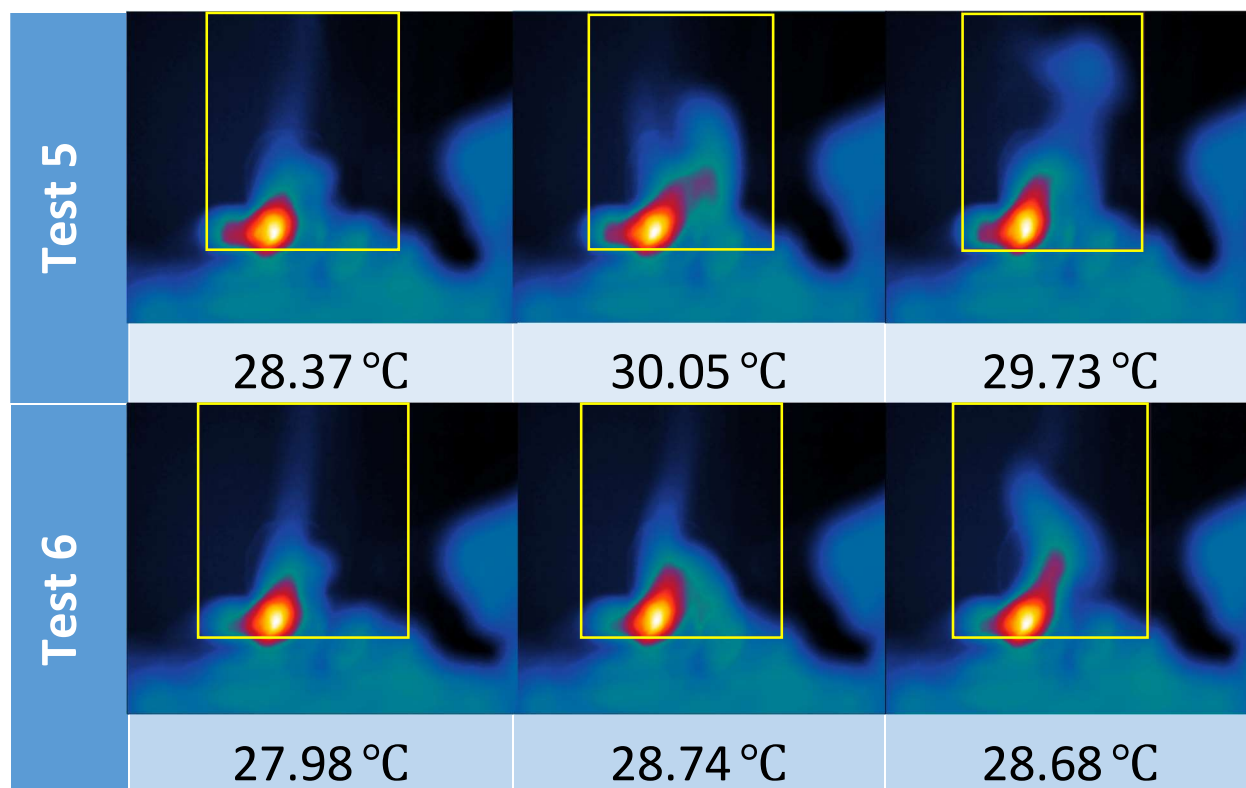
The frames from before and after the opening the lid were captured in the IR spectrum with the thermal imaging camera (TIC) to prove that there is no significant increase in temperature between the adjacent frames at 49 °C (when the flash point temperature is not reached).



**Figure S7a.** Images of the TIC and average temperature of the frame (yellow) before and after the opening of the lid at a temperature of 49 °C for three distinct tests.

The same experiment was performed at a temperature of 50 °C, to measure the increase of the average temperature between the two frames when a flash point occurs (figure S7b).

Decane 50°C			
	before	Flash point	after
Test 1			
	24.33 °C	25.75 °C	25.06 °C
Test 2			
	28.04 °C	29.10 °C	28.24 °C
Test 3			
	27.21 °C	28.17 °C	27.78 °C
Test 4			
	28.53 °C	29.65 °C	29.01 °C



**Figure S7b.** Images of the TIC and average temperature of the frame (yellow) before and after the opening of the lid at a temperature of 50 °C for six distinct tests.

The increase of the average temperature of the frames at 49 and 50 °C are presented in table S7.

Temperature (°C)	Test	Initial temperature (°C)	FP temperature (°C)	increase of temperature (%)	Average (%)
49	1	23.63	23.43	-0.9	-0.5
	2	24.30	24.20	-0.4	
	3	29.35	28.50	-0.2	
50	1	24.33	25.75	5.8	4
	2	28.04	29.10	3.8	
	3	27.21	28.17	3.5	
	4	28.53	29.65	3.9	
	5	28.37	30.05	5.9	
	6	27.98	28.74	2.7	

**Table S7.** Increase of the temperature before and after the opening of the lid of the decane standard (FP of 50 °C) at a temperature of 49 and 50 °C.

The average of increase in temperature between the frames before and after opening the lid is 4% of the initial temperature. Hence, when an increase in temperature between two frames is 4% or higher, a flash point is detected.

## S8 Glass transition temperature

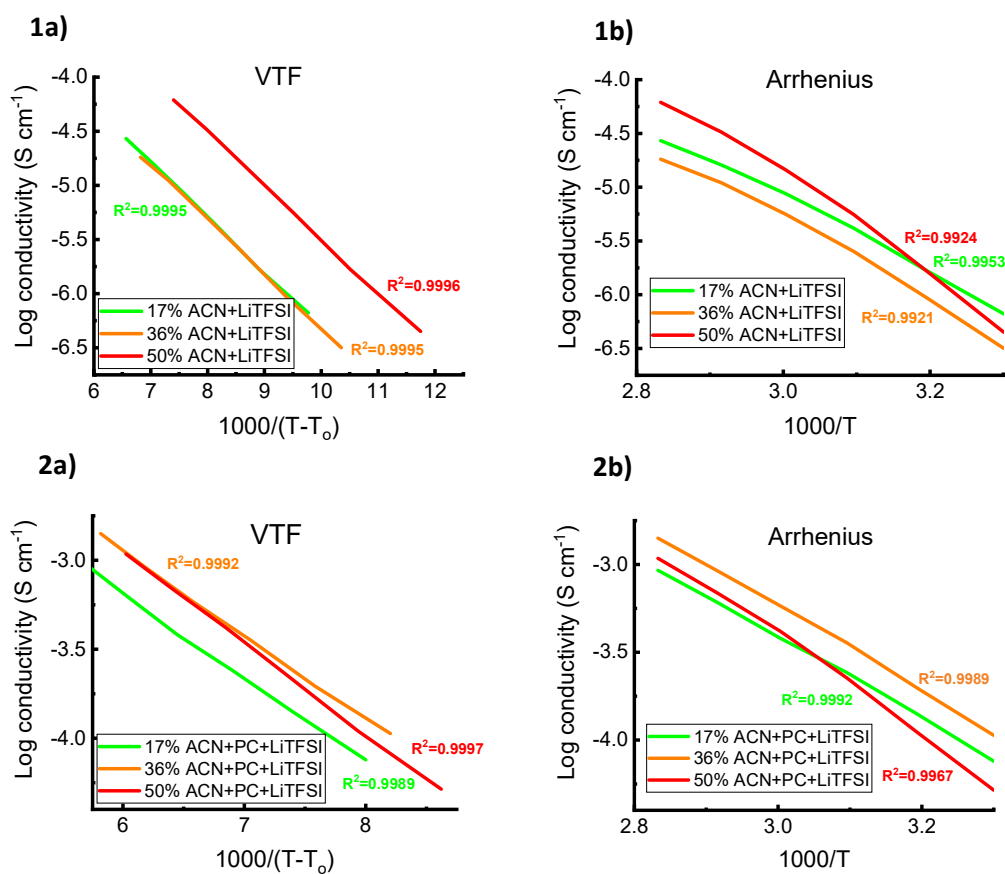
Differential scanning calorimetry (DSC 6000 PerkinElmer) was used to measure the glass transition ( $T_g$ ) temperature of different polymers. Samples were placed into a volatile Autosampler Aluminum Sample holder to avoid contact with the atmosphere. Two cycles from  $-65\text{ }^\circ\text{C}$  to  $40\text{ }^\circ\text{C}$  were made at a rate of  $5\text{ }^\circ\text{C}/\text{min}$  under  $\text{N}_2$ . The second cycle was used for the determination of the  $T_g$ .

sample	$T_g$ ( $^\circ\text{C}$ )
17% ACN	-41.5
36% ACN	-29.9
50% ACN	-14.5
17% ACN + PC	X*
36% ACN + PC	X*
50% ACN + PC	-39.3
17% ACN + LiTFSI	-22.3
36% ACN + LiTFSI	-16.6
50% ACN + LiTFSI	-5.1
17% ACN + LiTFSI + PC	X*
36% ACN + LiTFSI + PC	-41.9
50% ACN + LiTFSI + PC	-36.0

**Table S8.** Glass transition temperature of HNBR with different ACN content dry and with 20 wt% of PC with and without 24.5% wt% LiTFSI.

\*The glass transition temperature is below the limit of the instrument (below  $-45\text{ }^\circ\text{C}$ )

**S9 Arrhenius and Vogel-Tammann-Fulcher (VTF) plot of dry and gel polymers.**

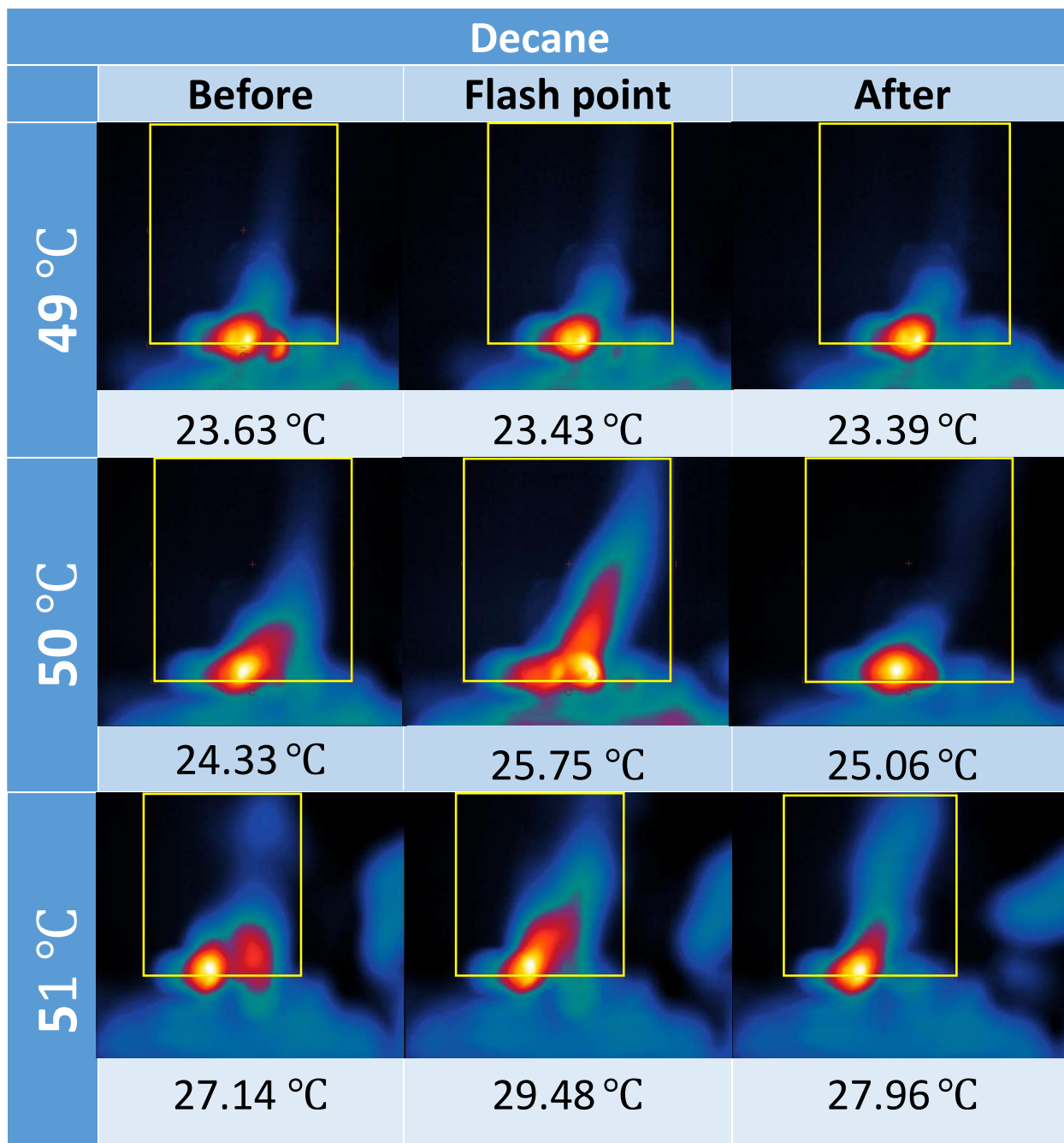


**Figure S9.** Conductivity of the dry polymers 1) and the gel-polymers 2) electrolyte represented with VTF a) and Arrhenius b) plot.

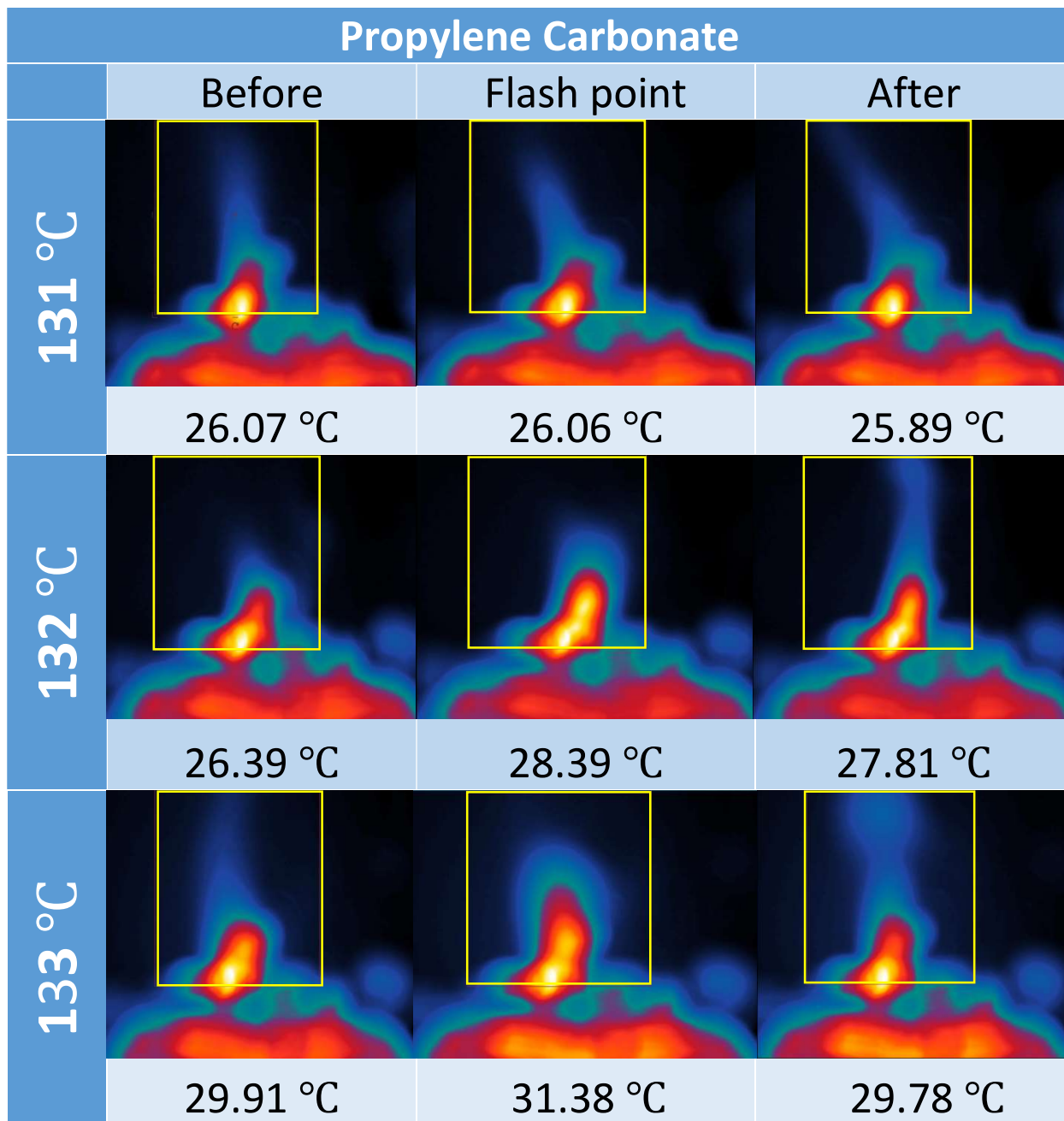
Sample	Activation energy (KJ/mol)	
	VTF	Arrhenius
17% ACN + LiTFSI	4.22	28.88
36% ACN + LiTFSI	4.19	31.52
50% ACN + LiTFSI	4.13	38.24
17% ACN + PC + LiTFSI	3.94	19.24
36% ACN + PC + LiTFSI	3.92	19.98
50% ACN + PC + LiTFSI	4.26	23.63

**Table S9.** Activation energy of the dry polymers and the gel polymers measured using the slope of the Arrhenius and VTF plots.

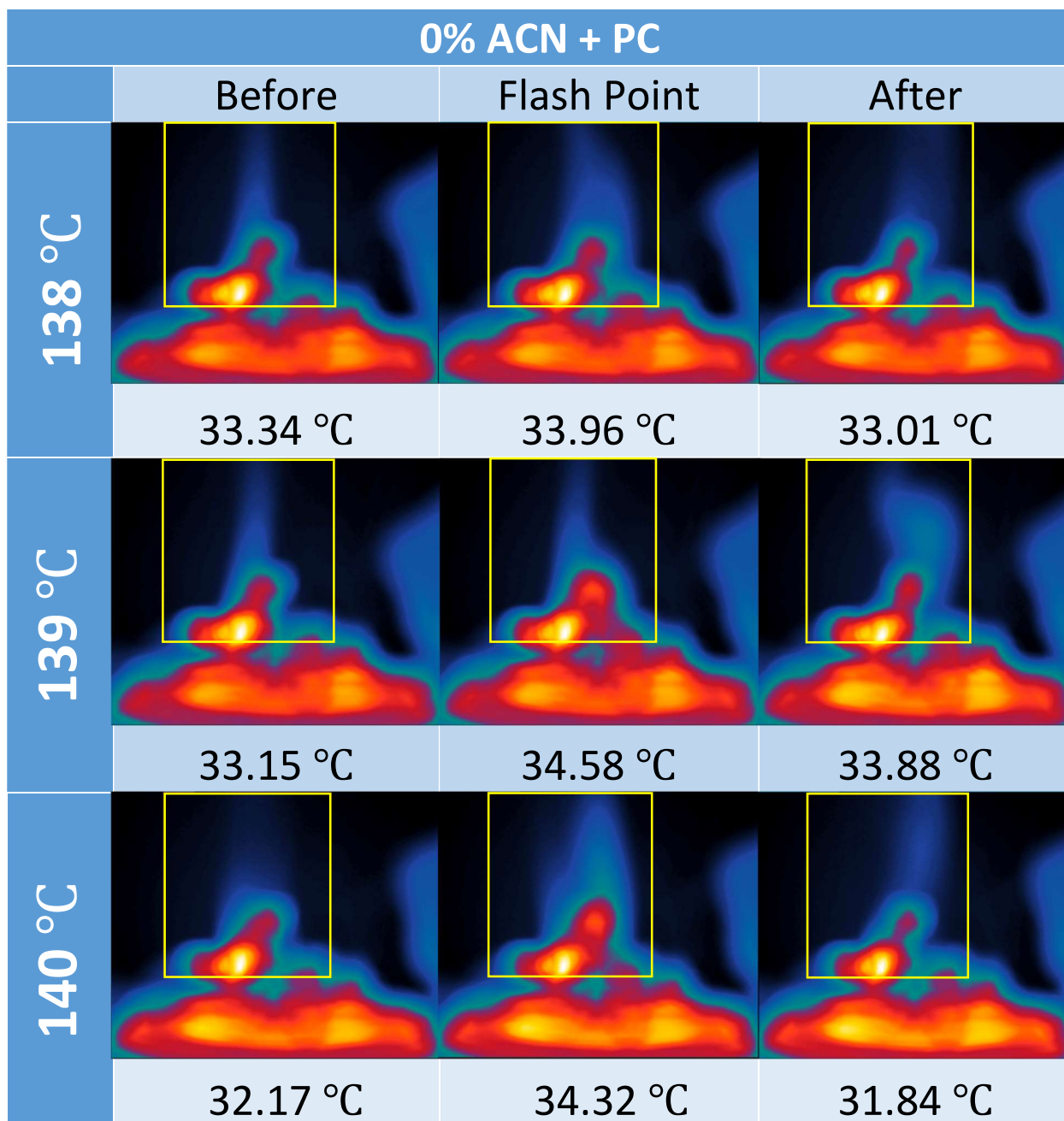
S10 Flash point results for the different samples analyzed.



**Figure S10a.** Images taken with the TIC camera and average temperature of the frame (in yellow) for the decane sample at the moment before, during and after the flash point occurred at a given temperature. The temperatures that were analyzed are: below the flash point, flash point temperature, above the FP temperature.

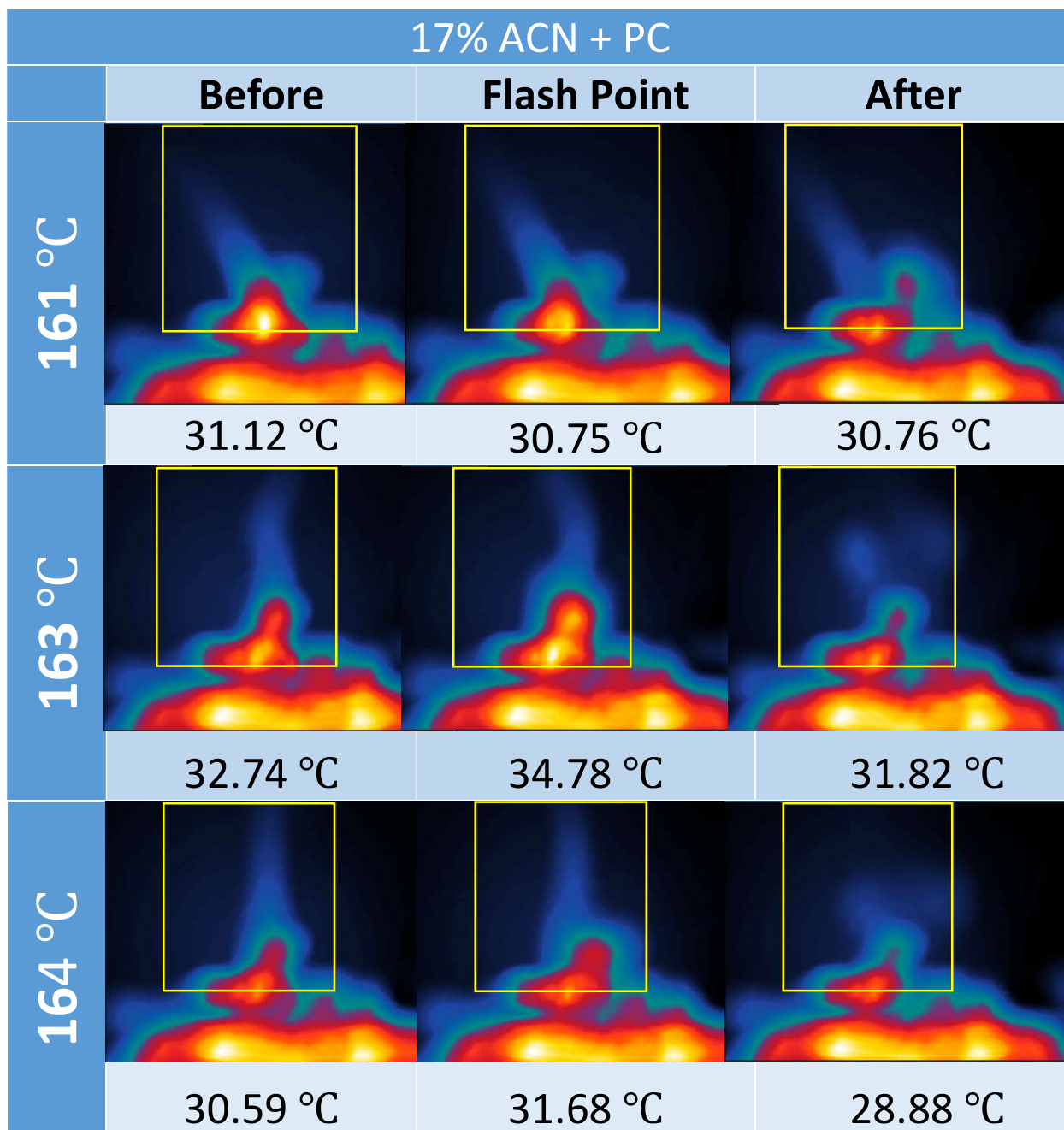


**Figure S10b.** Images taken with the TIC camera and average temperature of the frame (in yellow) for the sample propylene carbonate at the moment before, during and after the flash point occurred at a given temperature. The temperatures that were analyzed are: below the flash point, flash point temperature, above the FP temperature.

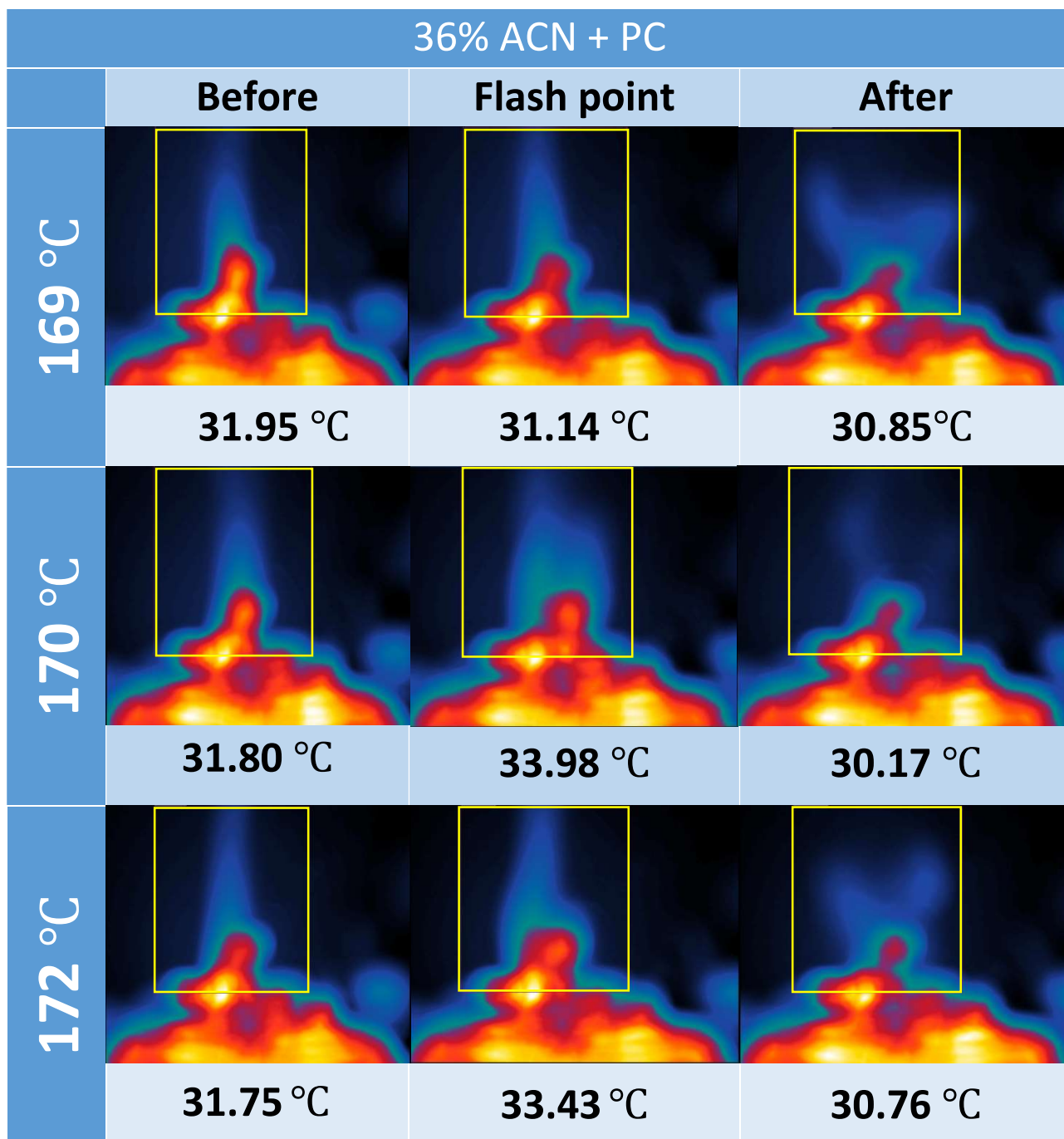


**Figure S10c.** Images taken with the TIC camera and average temperature of the frame (in yellow) for the sample 0% ACN with propylene carbonate at the moment before, during and after the flash point occurred at a given temperature. The temperatures that were analyzed are: below the flash point, flash point temperature, above the FP temperature.

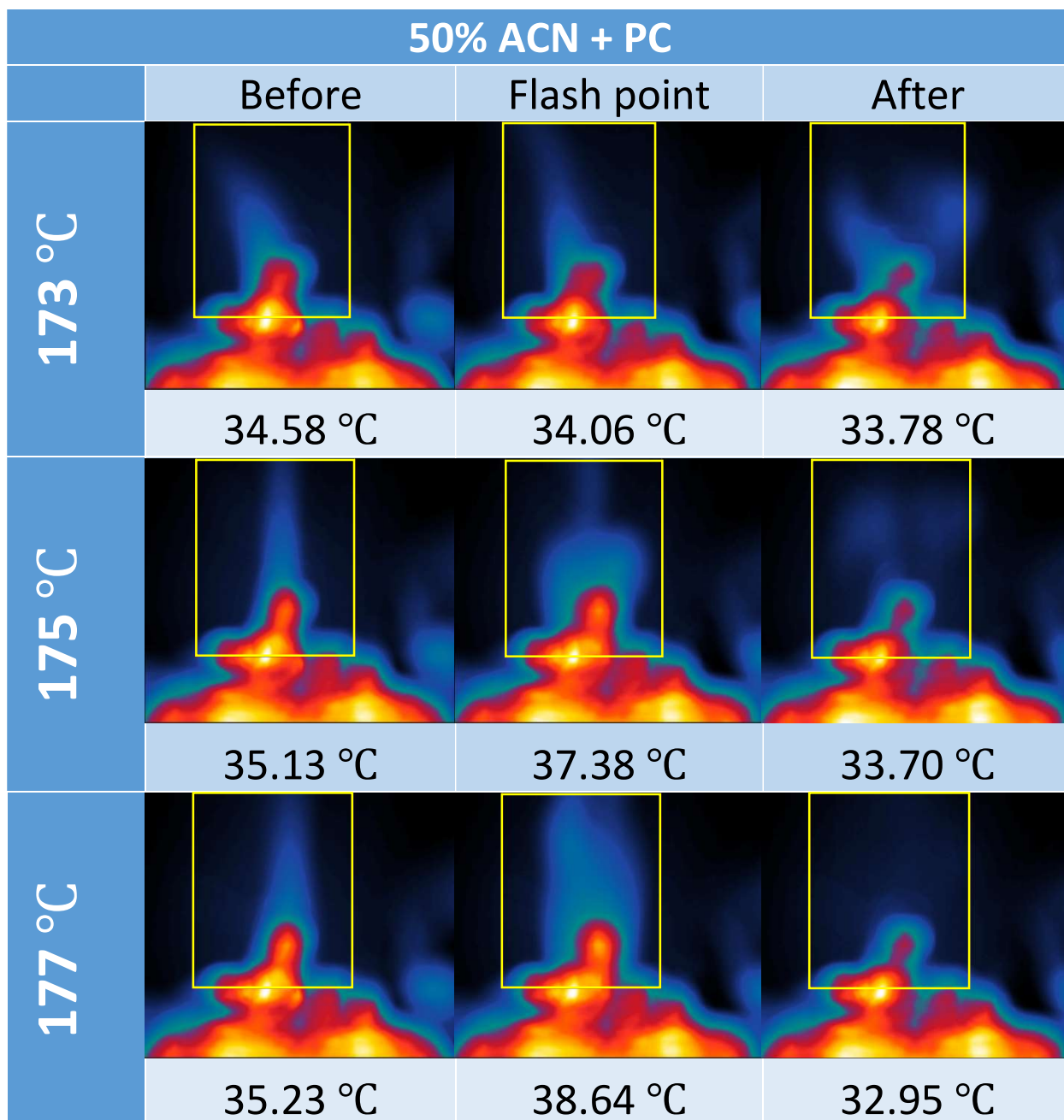




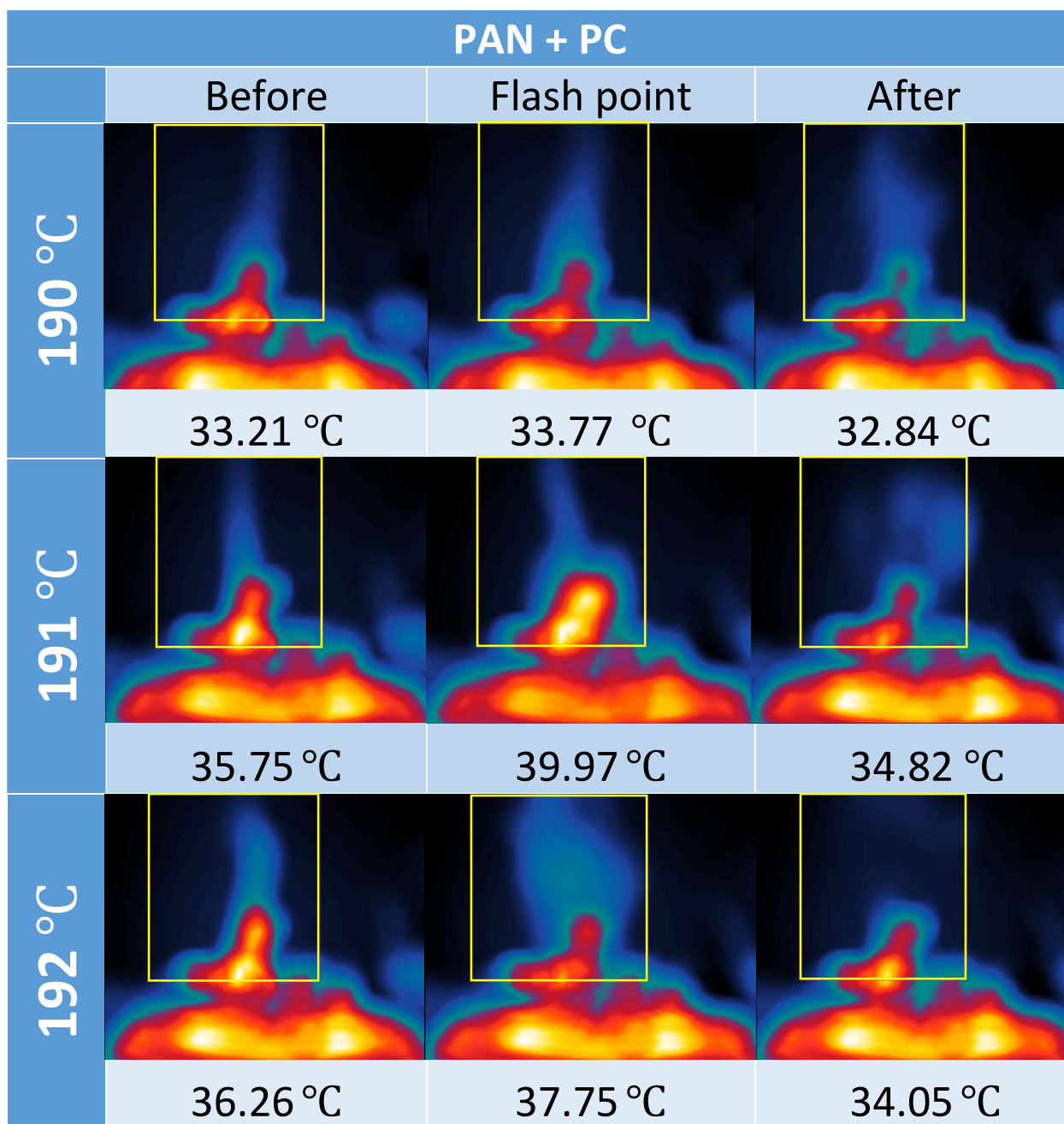
**Figure S10d.** Images taken with the TIC camera and average temperature of the frame (in yellow) for the sample 17% ACN with propylene carbonate at the moment before, during and after the flash point occurred at a given temperature. The temperatures that were analyzed are: below the flash point, flash point temperature, above the FP temperature.



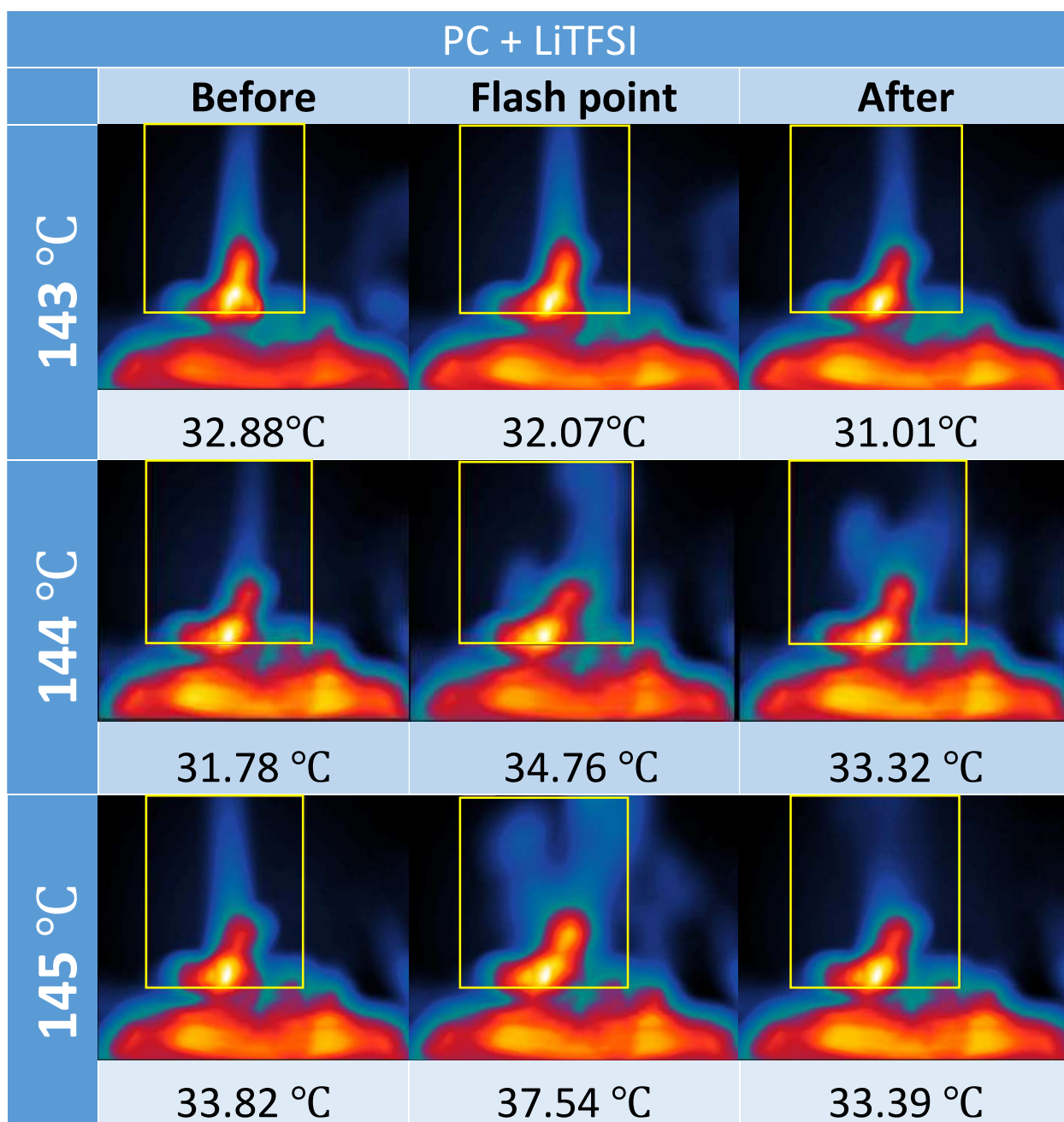
**Figure S10e.** Images taken with the TIC camera and average temperature of the frame (in yellow) for the sample 36% ACN with propylene carbonate at the moment before, during and after the flash point occurred at a given temperature. The temperatures that were analyzed are: below the flash point, flash point temperature, above the FP temperature.



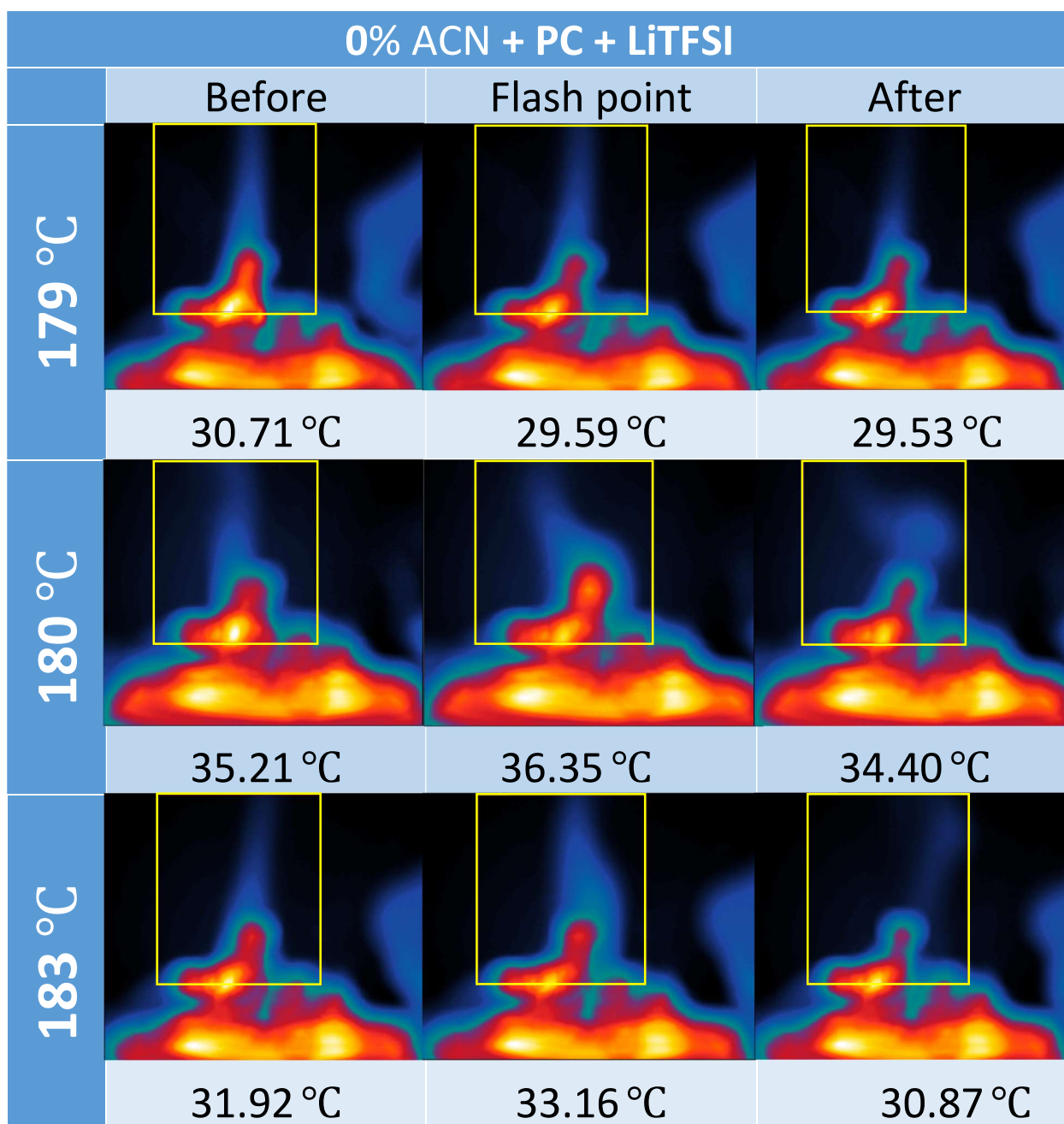
**Figure S10f.** Images taken with the TIC camera and average temperature of the frame (in yellow) for the sample 50% ACN with propylene carbonate at the moment before, during and after the flash point occurred at a given temperature. The temperatures that were analyzed are: below the flash point, flash point temperature, above the FP temperature.



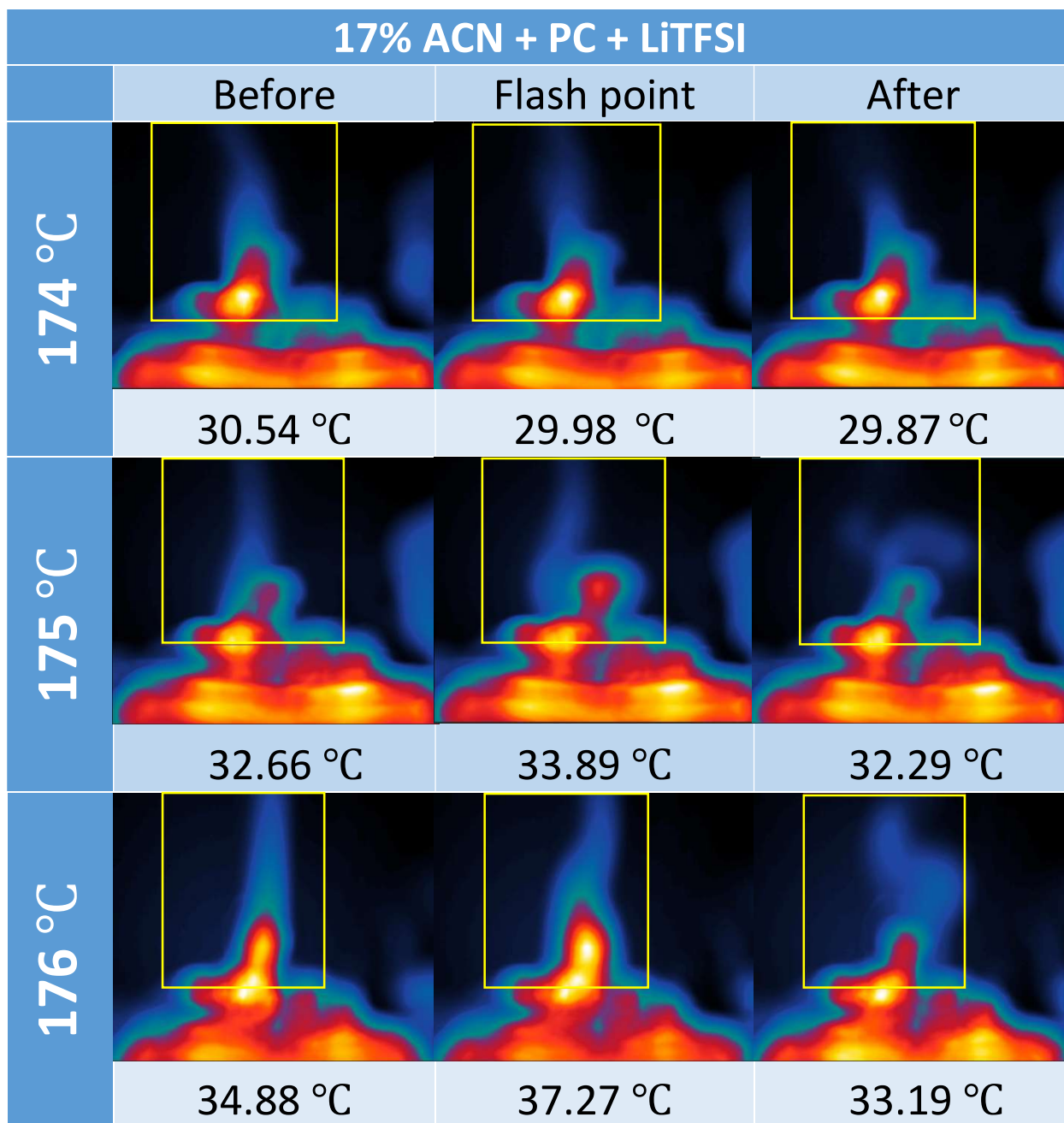
**Figure S10g.** Images taken with the TIC camera and average temperature of the frame (in yellow) for the sample polyacrylonitrile with propylene carbonate at the moment before, during and after the flash point occurred at a given temperature. The temperatures that were analyzed are: below the flash point, flash point temperature, above the FP temperature.



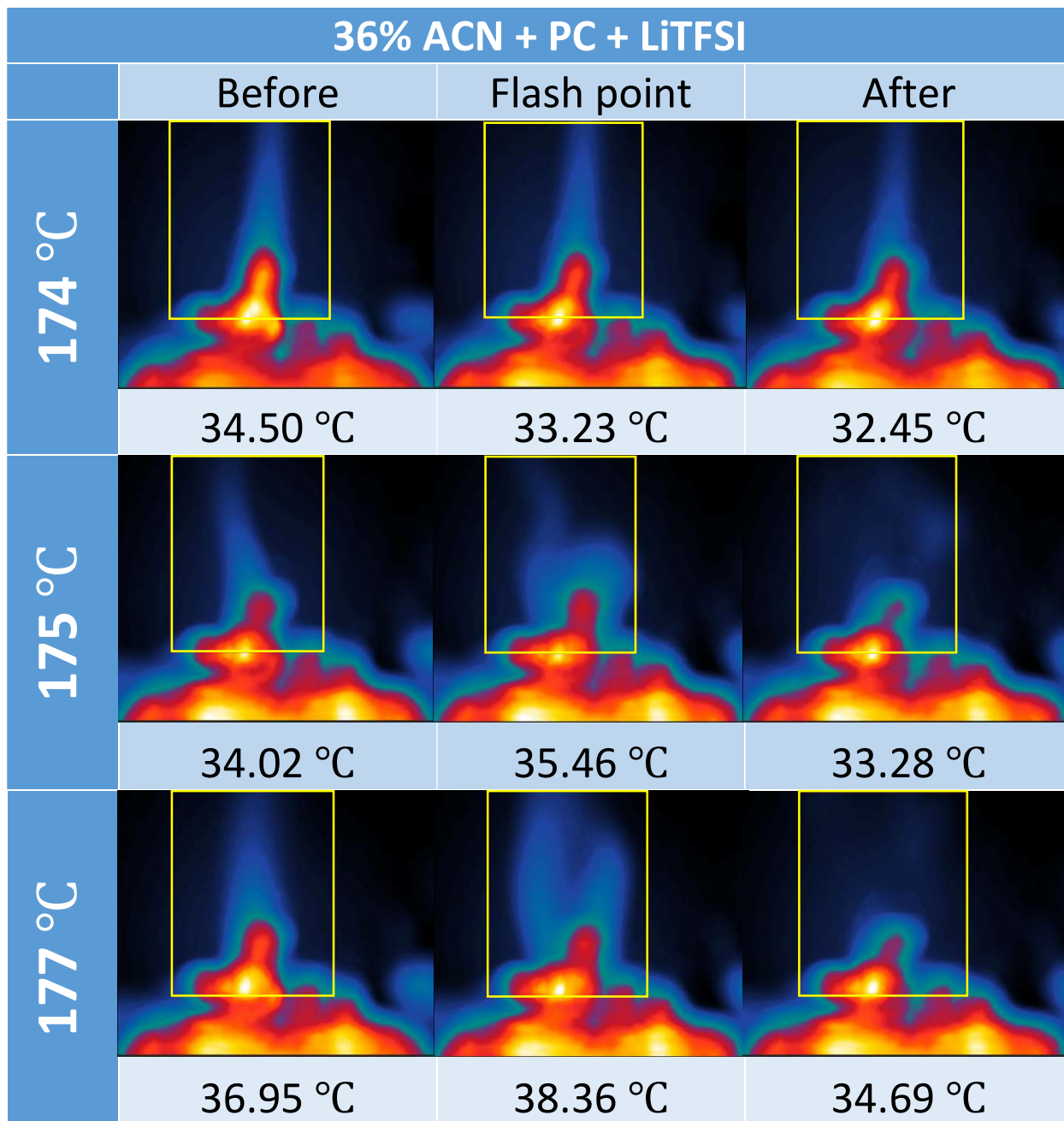
**Figure S10h.** Images taken with the TIC camera and average temperature of the frame (in yellow) for the sample propylene carbonate with LiTFSI at the moment before, during and after the flash point occurred at a given temperature. The temperatures that were analyzed are: below the flash point, flash point temperature, above the FP temperature.



**Figure S10i.** Images taken with the TIC camera and average temperature of the frame (in yellow) for the sample 0% ACN with propylene carbonate and LiTFSI at the moment before, during and after the flash point occurred at a given temperature. The temperatures that were analyzed are: below the flash point, flash point temperature, above the FP temperature.

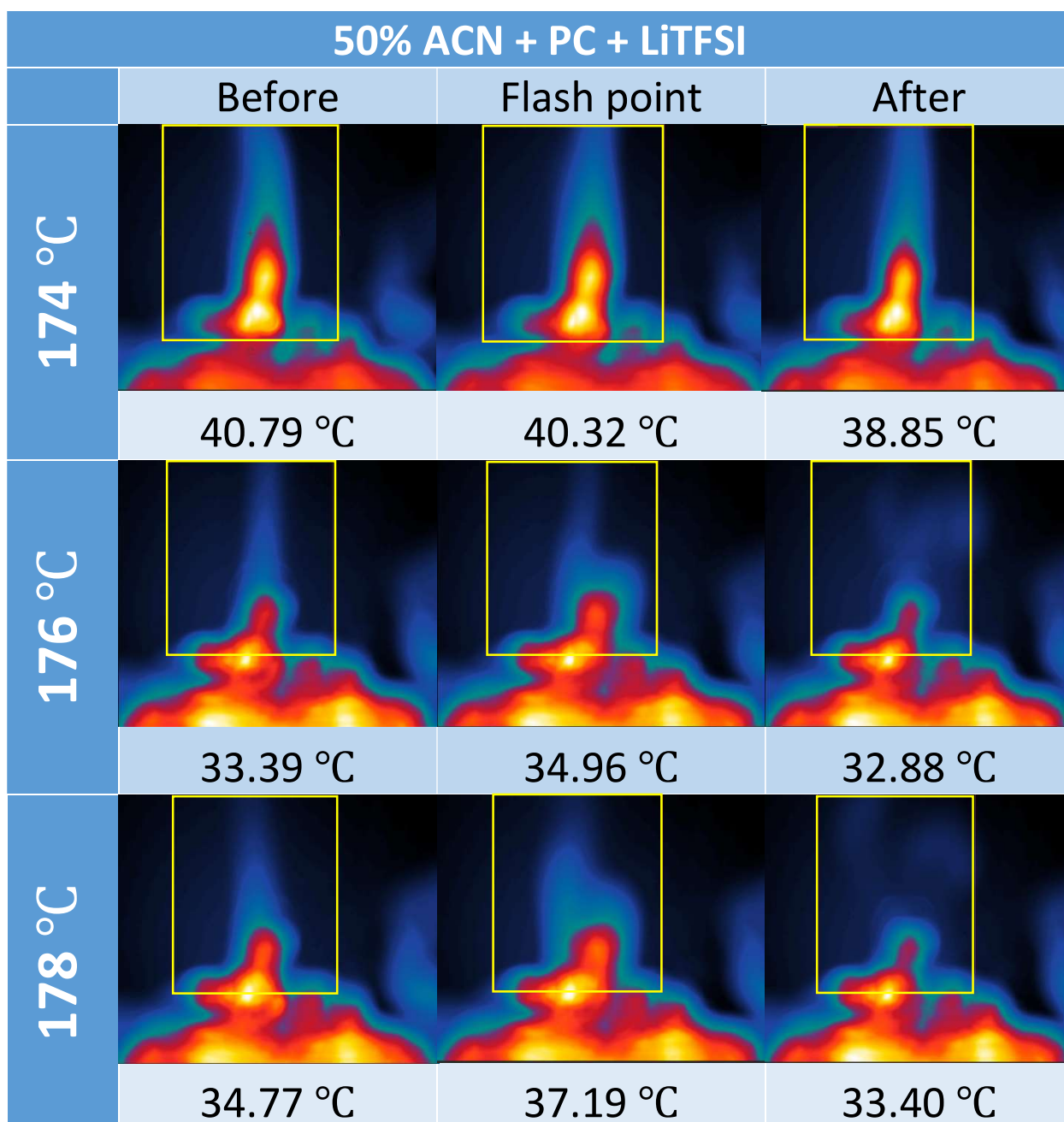


**Figure S10j.** Images taken with the TIC camera and average temperature of the frame (in yellow) for the sample 17%ACN with propylene carbonate and LiTFSI at the moment before, during and after the flash point occurred at a given temperature. The temperatures that were analyzed are: below the flash point, flash point temperature, above the FP temperature.

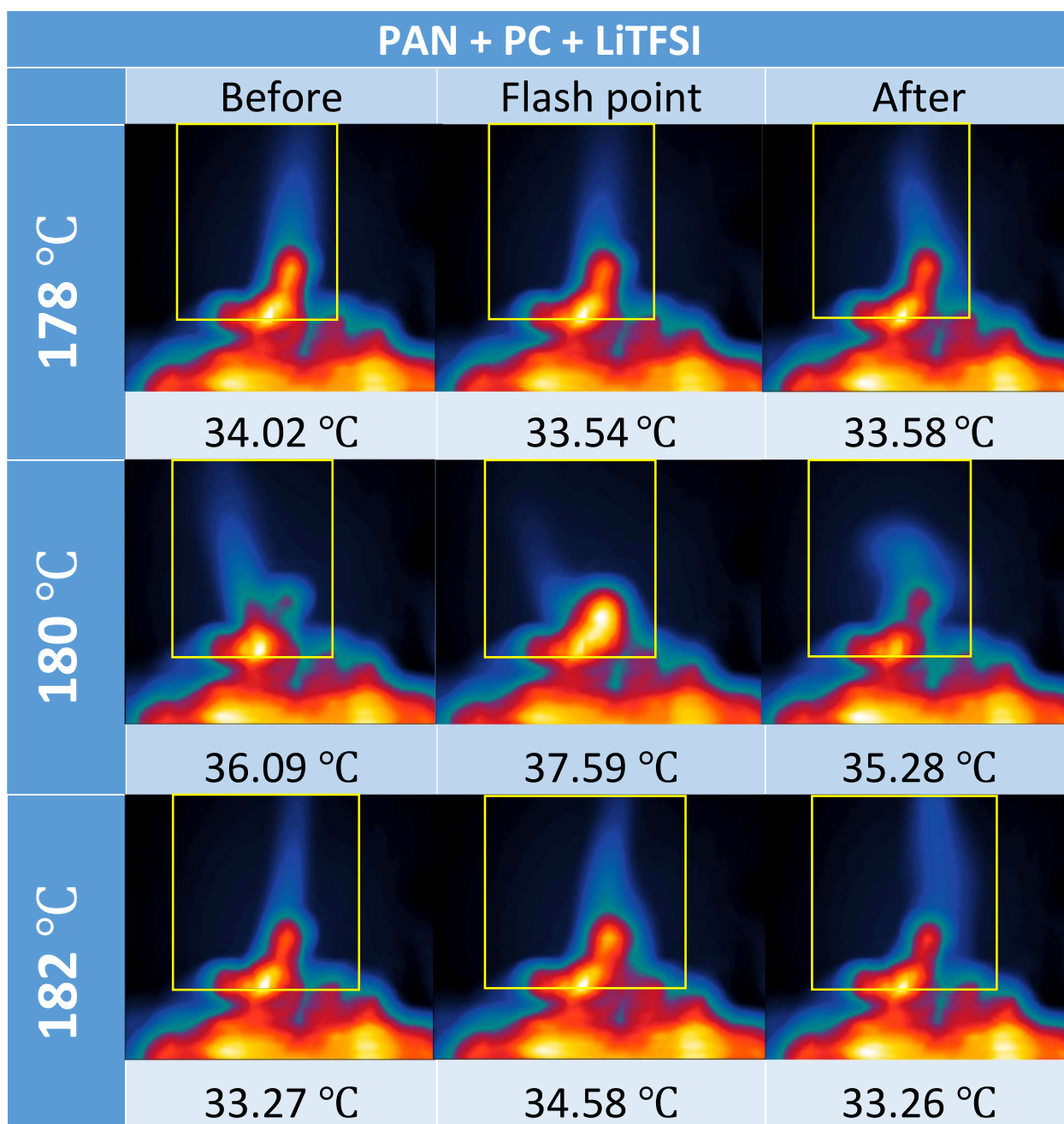


**Figure S10k.** Images taken with the TIC camera and average temperature of the frame (in yellow) for the sample 36% ACN with propylene carbonate and LiTFSI at the moment before, during and after the flash point occurred at a given temperature. The temperatures that were analyzed are: below the flash point, flash point temperature, above the FP temperature.





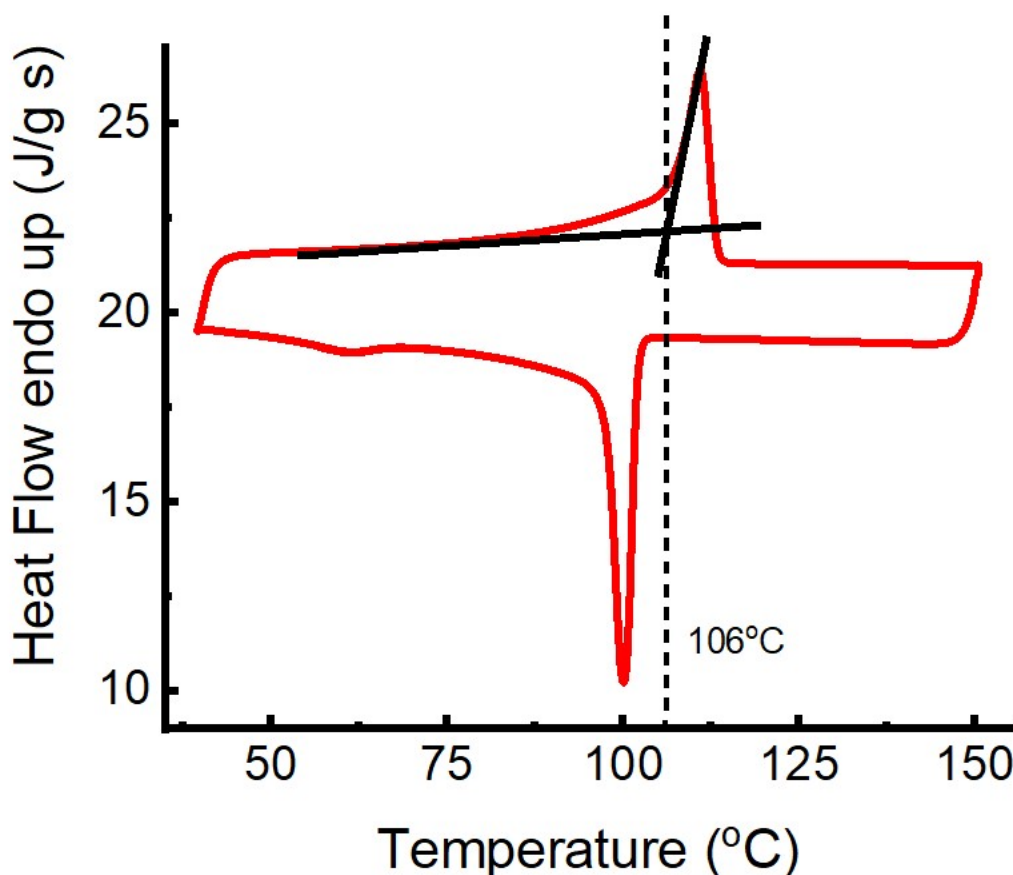
**Figure S10I.** Images taken with the TIC camera and average temperature of the frame (in yellow) for the sample 50% ACN with propylene carbonate and LiTFSI at the moment before, during and after the flash point occurred at a given temperature. The temperatures that were analyzed are: below the flash point, flash point temperature, above the FP temperature.



**Figure S10m.** Images taken with the TIC camera and average temperature of the frame (in yellow) for the sample polyacrylonitrile with propylene carbonate and LiTFSI at the moment before, during and after the flash point occurred at a given temperature. The temperatures that were analyzed are: below the flash point, flash point temperature, above the FP temperature.

### S11 Melting Point of Polyethylene via DSC

Differential scanning calorimetry (DSC 6000 PerkinElmer) was used to measure the melting point of polyethylene. Samples were placed into a volatile Autosampler Aluminum Sample holder to avoid contact with the atmosphere. Two cycles from 40 °C to 150 °C were made at a rate of 5 °C/min under N<sub>2</sub>. The second cycle was used for the determination of the melting point.

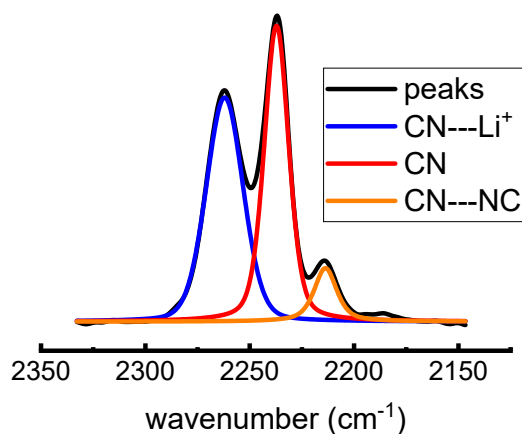


**Figure S11.** Second cycle of the DSC measurement of polyethylene between 40 °C to 150 °C to determine the melting point of the polymer.

The melting point of polyethylene is 106 °C. The flash point measurements are done at temperature higher than the melting point of polyethylene.

## S12 Interactions of nitrile with lithium salt analyzed with FT-IR

Figure S12 represent an example of the deconvolution of the nitrile peaks using a mix of Lorentzian and Gaussian functions.



**Figure S12.** Example of the deconvolution of the nitrile peaks: CN---Li<sup>+</sup>, CN and CN---NC.

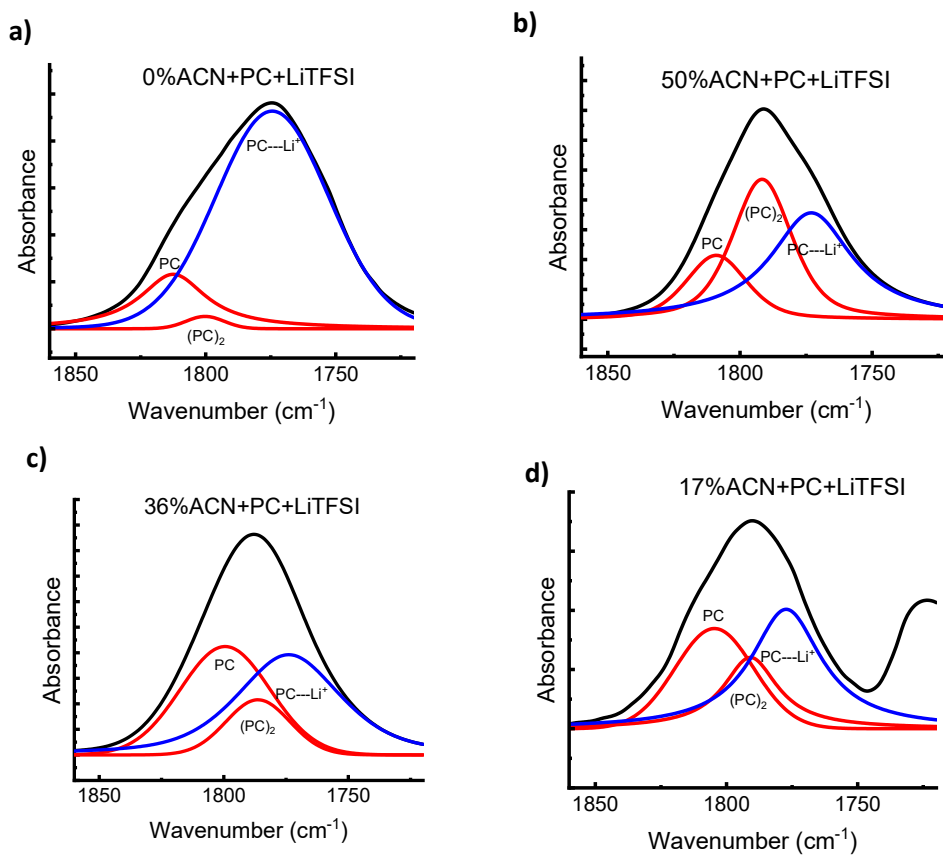
For each dry polymer and gel polymer containing lithium salt, the ratio between the integral of the peak representing the interaction of the nitrile with the lithium and the peak of the nitrile was calculated. All calculations take the average of 3 spectra into consideration. Results are presented in Table S12:

Name	Amount of ACN (%)	$\frac{C \equiv N - - Li^+}{C \equiv N}$	Standard deviation
ACN + LiTFSI	17	1.9	0.1
	36	1.25	0.1
	50	0.85	0.01
ACN + LiTFSI + PC	17	1.05	0.09
	36	0.93	$4 * 10^{-4}$
	50	0.84	0.04

**Table S12.** Ratio of C≡N---Li<sup>+</sup> for one unit of C≡N for the different polymeric matrices of HNBR containing 17, 36 and 50% ACN with and without PC. Salt and PC mass ratios are held constant at 24.5 wt% and 20 wt% respectively.

### S13 deconvolution of the carbonyl peak for the different polymeric matrices.

Carbonyl peaks of different gel-polymer electrolytes were deconvoluted into the three main carbonyl interactions: the vibration of the PC monomer, the vibration of the PC dimer and the vibration related to the interaction between the PC and the lithium salt.



**Figure S13.** Deconvolution of the carbonyl peak into three principal vibrations: PC monomers, PC dimers and PC interaction with lithium ions for a) 0% ACN + PC + LiTFSI, b) 17% ACN + PC + LiTFSI, c) 36% ACN + PC + LiTFSI, d) 50% ACN + PC + LiTFSI.

Figure S13 clearly shows the interaction of the PC with the lithium ion. The PC---Li<sup>+</sup> interaction is stronger for 0% ACN + PC + LiTFSI as there is no competition with lithium-nitrile interactions.