

Supplementary Materials for

Solution-processed transparent ferroelectric nylon thin films

Saleem Anwar, Daniel Pinkal, Wojciech Zajaczkowski, Philipp von Tiedemann, Hamed Sharifi Dehsari, Manasvi Kumar, Thomas Lenz, Ulrike Kemmer-Jonas, Wojciech Pisula, Manfred Wagner, Robert Graf, Holger Frey, Kamal Asadi*

*Corresponding author. Email: asadi@mpip-mainz.mpg.de

Published 16 August 2019, *Sci. Adv.* **5**, eaav3489 (2019)
DOI: 10.1126/sciadv.aav3489

This PDF file includes:

- Fig. S1. *D-E* hysteresis loop and switching current of MQS nylon-11.
- Fig. S2. ¹³C solution NMR spectra of the TFA:acetone-*d*₆ mixture.
- Fig. S3. ¹H solution NMR spectra of the TFA:acetone-*d*₆ mixture.
- Fig. S4. ¹H-NMR DOSY measurement (850.3 MHz at 298 K) of nylon-11 solution in pure TFA (red spectrum) and 50:50 mol % mixture of TFA:acetone-*d*₆ (black spectrum).
- Fig. S5. Haze as a function of film thickness of nylon-11.
- Fig. S6. DSC curves of SQ and MQS nylon-11 films.
- Fig. S7. Room-temperature FTIR spectra of the SQ thin film compared with MQS film of nylon-11.
- Fig. S8. WAXD pattern of the MQS film along the parallel and perpendicular to the stretch direction.
- Table S1. Literature overview of the crystalline phases of nylon-11 at room temperature.
- Table S2. Comparing the ferroelectric properties, P_r , and E_C of nylon-11 and nylon-5 with those of PVDF and P(VDF-TrFE) reported in literature.
- References (34–44)

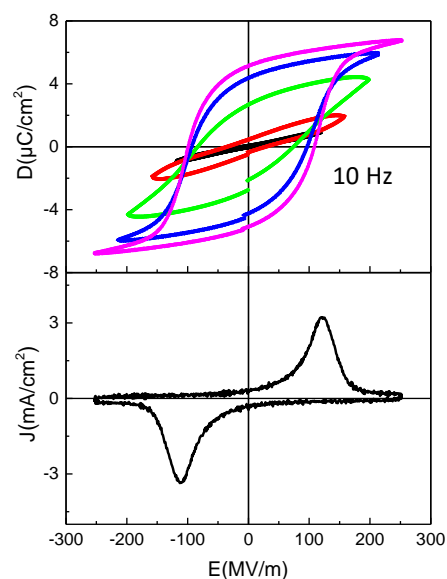


Fig. S1. *D-E* hysteresis loop and switching current of MQS nylon-11.

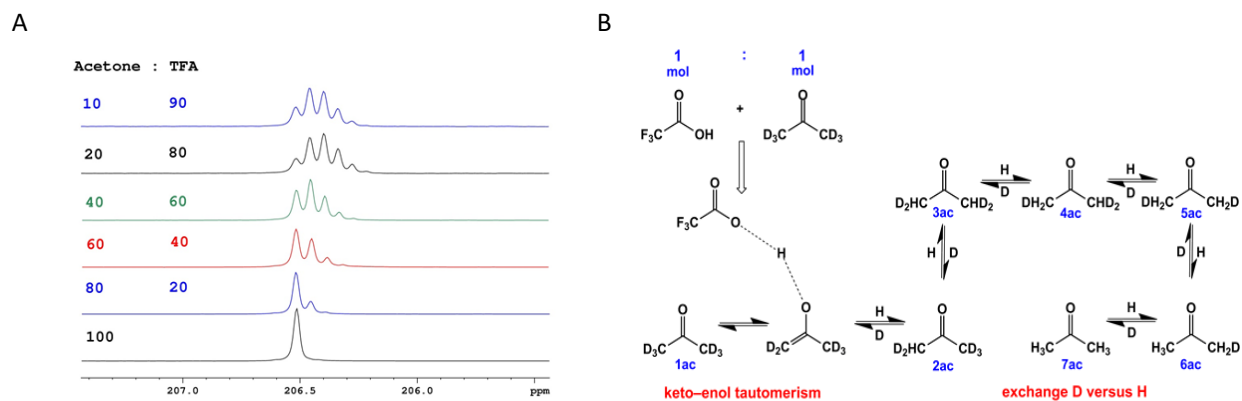
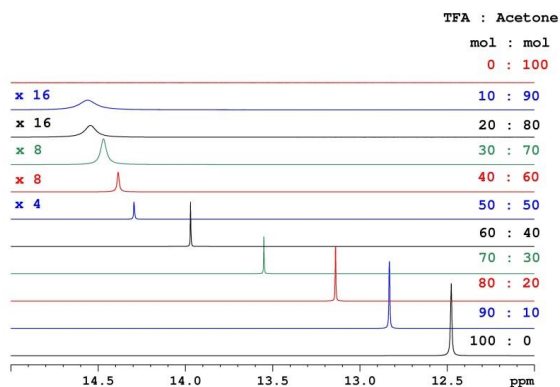


Fig. S2. ^{13}C solution NMR spectra of the TFA:acetone- d_6 mixture. (A) The spectra (213.8 MHz at 298K) of different mixtures of TFA:acetone- d_6 . All spectra are recalibrated to the 100 % acetone- d_6 signal at 206.3 ppm. (B) Scheme: the induced exchange of deuterium with a proton via the keto-enol-tautomerism. Seven different compounds (1ac, 2ac...7ac) of acetone H/D exchange molecules exist and at least six of them can be detected.

A



B

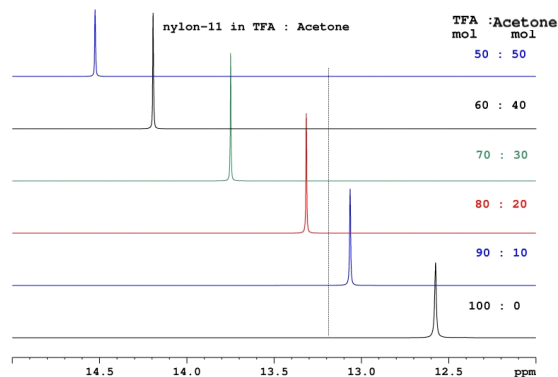


Fig. S3. ^1H solution NMR spectra of the TFA:acetone- d_6 mixture. (A) (850.3 MHz at 298K) of different mixtures of TFA:acetone- d_6 . **(B)** ^1H NMR (850.3 MHz at 298K) of nylon-11 solution in different TFA:acetone- d_6 solvent mixtures. The chemical shift calibration for proton spectra was done with an external capillary filled with $\text{C}_2\text{D}_2\text{HCl}_4$ (5.93 ppm) inside the different samples tubes.

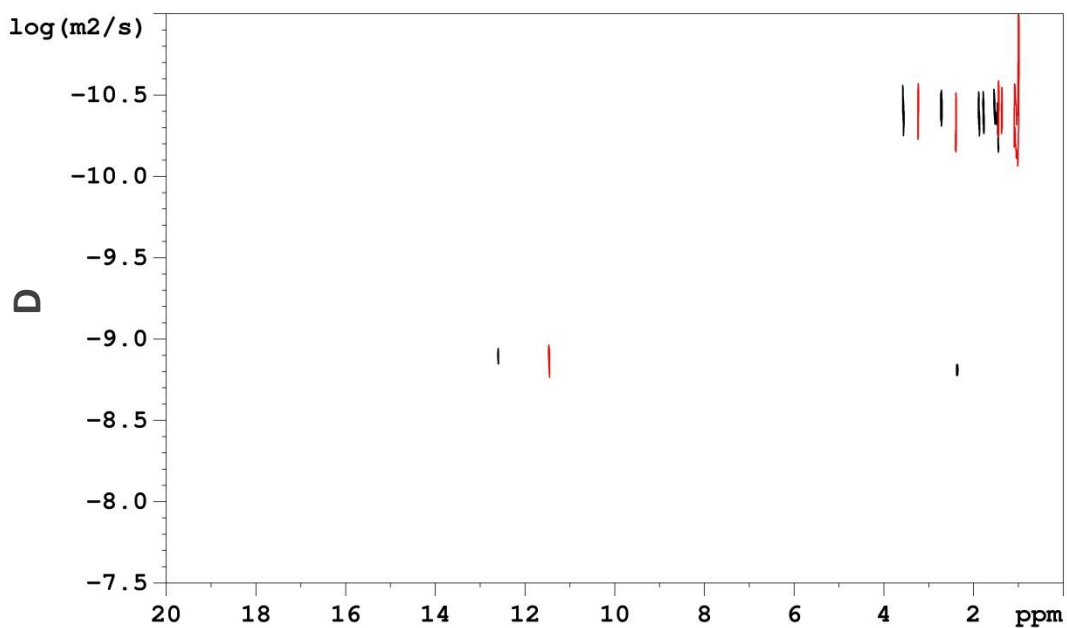


Fig. S4. ^1H -NMR DOSY measurement (850.3 MHz at 298 K) of nylon-11 solution in pure TFA (red spectrum) and 50:50 mol % mixture of TFA:acetone- d_6 (black spectrum). The chemical shift calibration was done with an external capillary filled with C_2HDCl_4 (5.93 ppm).

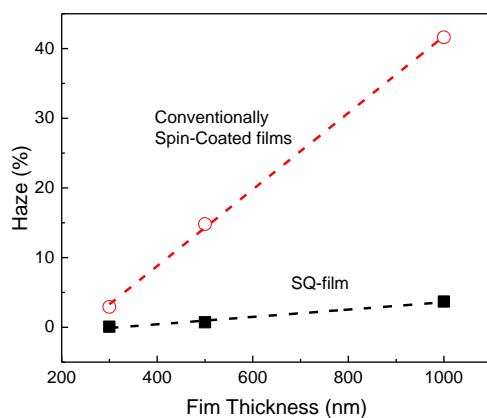


Fig. S5. Haze as a function of film thickness of nylon-11. The conventional spin-coated and the SQ thin films are compared. The dash lines are a guide to the eye.

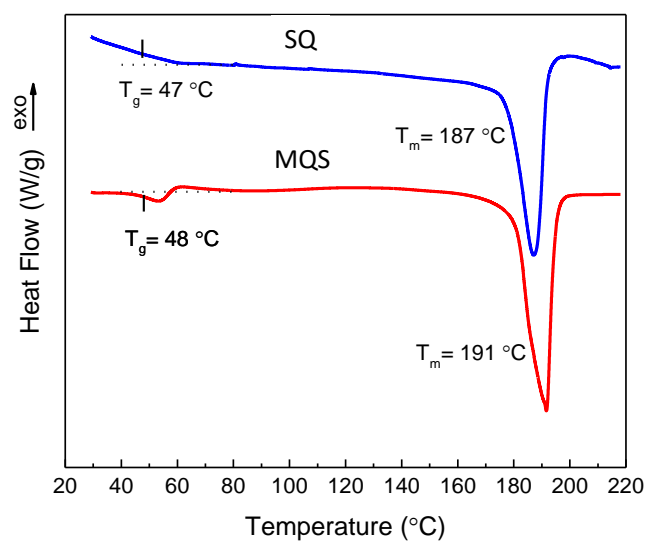


Fig. S6. DSC curves of SQ and MQS nylon-11 films.

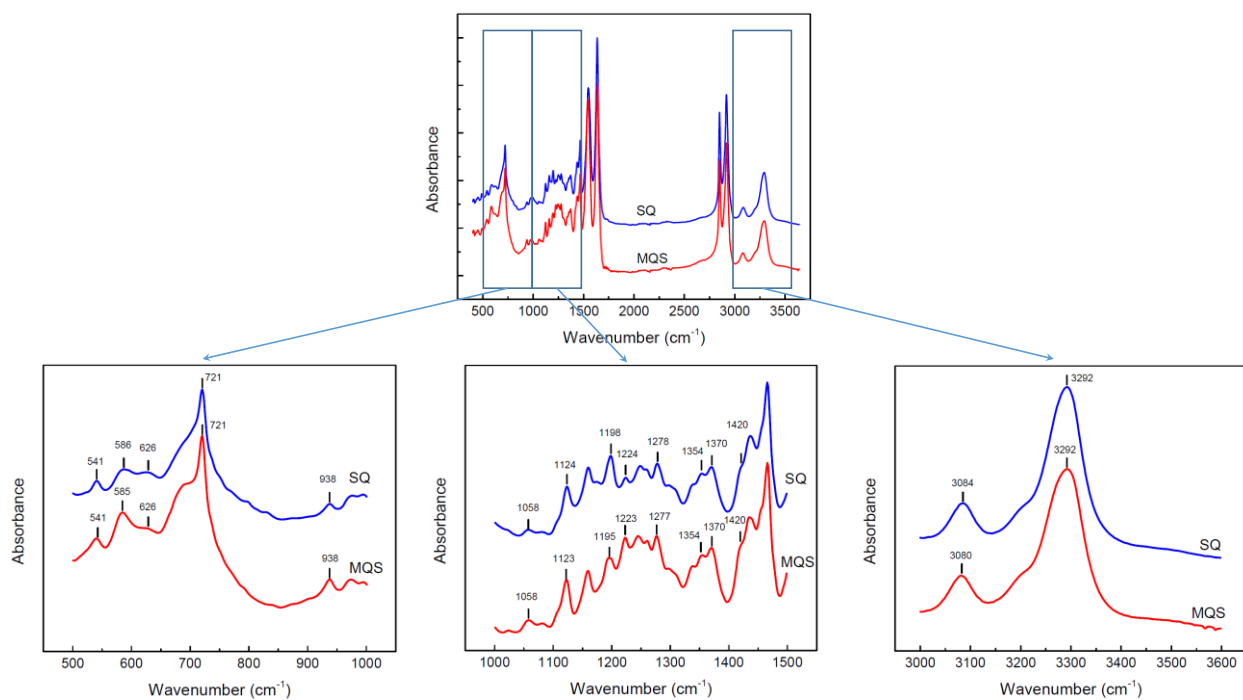


Fig. S7. Room-temperature FTIR spectra of the SQ thin film compared with MQS film of nylon-11.

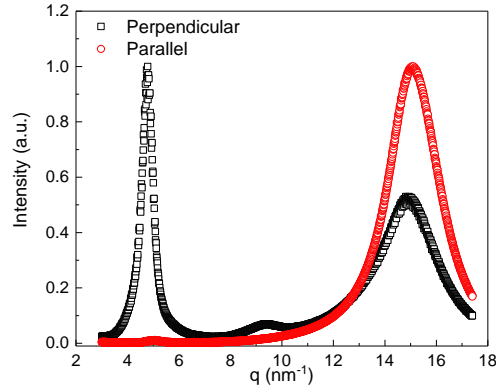


Fig. S8. WAXD pattern of the MQS film along the parallel and perpendicular to the stretch direction.

Table S1. Literature overview of the crystalline phases of nylon-11 at room temperature.

Phase	Ref.	(001)			(100)			(010)		
		2θ ($^{\circ}$ D)	q (nm^{-1})	d -spacing (nm)	2θ ($^{\circ}$ D)	q (nm^{-1})	d -spacing (nm)	2θ ($^{\circ}$ D)	q (nm^{-1})	d -spacing (nm)
α	(20)	7.5	-	1.17	19.9	-	0.445	23.7	-	0.374
	(7)	7.4	-	1.19	20.2	-	0.439	22.9	-	0.388
	(15)	-	5.62	1.11	-	14.50	0.433	-	16.96	0.370
	(38)	-	-	-	-	-	0.44	-	-	0.37
	(39)	-	-	1.133	-	-	0.444	-	-	0.372
	(40)	-	-	1.19	-	-	0.433	-	-	0.372
	(41)	-	-	1.133	-	-	0.444	-	-	0.372
	(42)	-	-	-	-	-	0.437	-	-	0.382
α'	(20)	7.2	-	1.227	20.2	-	0.440	23.1	-	0.384
	(7)	7.4	-	1.19	21.1	-	0.421	22.9	-	0.388
	(39,41)	-	-	1.195	-	-	4.40	-	-	0.382
	(9)	-	-	-	21	-	-	23	-	0.392
γ	(20)	5.9	-	1.49	21.3	-	0.416	21.8	-	0.406
	(15,3)	-	4.27	1.47	-	15.08	0.417	-	15.85	0.396
	(40)	-	-	1.44	-	-	-	-	0.408	-
γ'	(22)	5.97*	-	1.48	21.5	-	-	-	0.410	-
δ'	(20)	7.1	-	1.24	21.4	-	-	-	0.414	-
	(3)	-	4.8	1.306	-	14.75	-	-	0.426	-
	(9,22,43)	-	-	-	-	-	-	-	0.416	-
	(44)	6.8	-	1.299	21.1	-	-	-	0.421	-
	(38)	-	-	-	-	-	-	-	0.420	-
	(40)	-	-	-	-	-	-	-	0.411	-
This work	MQS	-	4.79	1.311	-	15.08	-	-	0.417	-
	SQ	-	4.79	1.311	-	15.30	-	-	0.411	-

* Reported for 002, which is the second order reflection of 001 peak

Table S2. Comparing the ferroelectric properties, P_r , and E_c of nylon-11 and nylon-5 with those of PVDF and P(VDF-TrFE) reported in literature.

Ferroelectric Polymer	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (MV/m)	P_r @ 10^6 cycles * ($\mu\text{C}/\text{cm}^2$)	P_r @ 10^6 cycles ‡ ($\mu\text{C}/\text{cm}^2$)
PVDF (δ -Phase) (34)	7.0	115	6.1	N.R.
PVDF (β -Phase) (35)	5.8*	90	N.R.	N.R.
PVDF (β -Phase) (35)	6.3†	90	N.R.	N.R.
P(VDF-TrFE)				
50/50 (36)	4.7	65	N.R.	N.R.
65/35 (29)	7.0	60	2.5	3.3
70/30 (37)	6.3	65	0.8	N.R.
80/20 (36)	6.5	82	N.R.	N.R.
Nylon-5 MQS (4)	12.5	125	N. R.	N.R.
Nylon-11 SQ (this work)	4.5	200	4.5	4.5

N.R. stands for not reported.

* uni-axially oriented PVDF film.

† bi-axially oriented PVDF film.

* P_r measured without applying any resting time between two consecutive pulses.

‡ P_r measured after applying a resting time of 5 seconds between two consecutive pulses.