Supporting Information: Stretched Poly(acrylonitrile) as a Scalable Alignment Medium for DMSO

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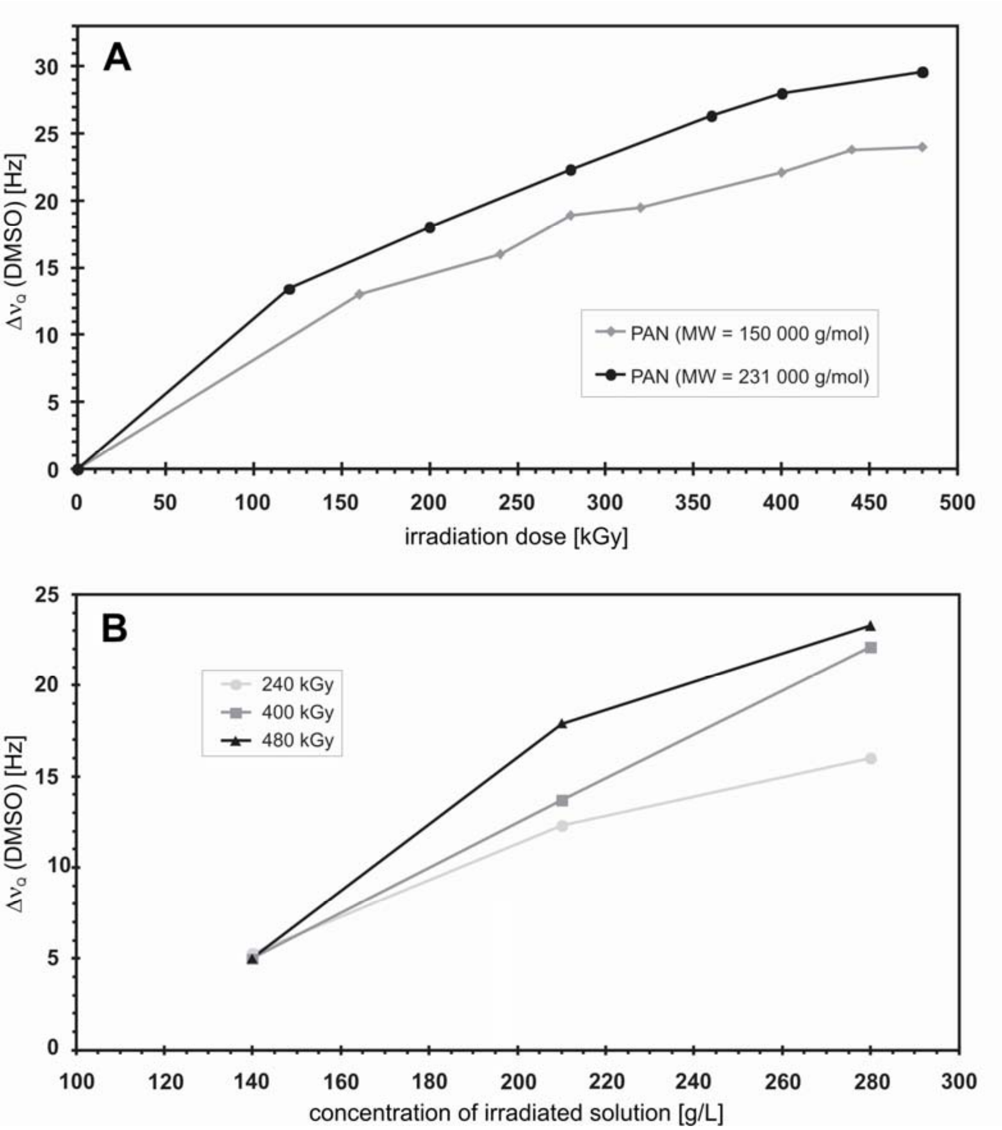


Figure S1. Scalability of alignment. (A) Quadrupolar splitting $\Delta\nu_Q$ of PAN/DMSO-gels with respect to the irradiation dose applied for cross-linking. All gels were cross-linked inside the NMR-tube as a 280 g/L PAN/DMSO-d_6 solution. Linear polymers of two different molecular weights have been used. (B) Quadrupolar splitting $\Delta\nu_Q$ of various gels with respect to the initial concentration of the PAN (MW=150000 g/mol)/DMSO-d_6 solution used for irradiation with accelerated electrons. All samples were measured after 57 days of equilibration in silylated NMR-tubes.

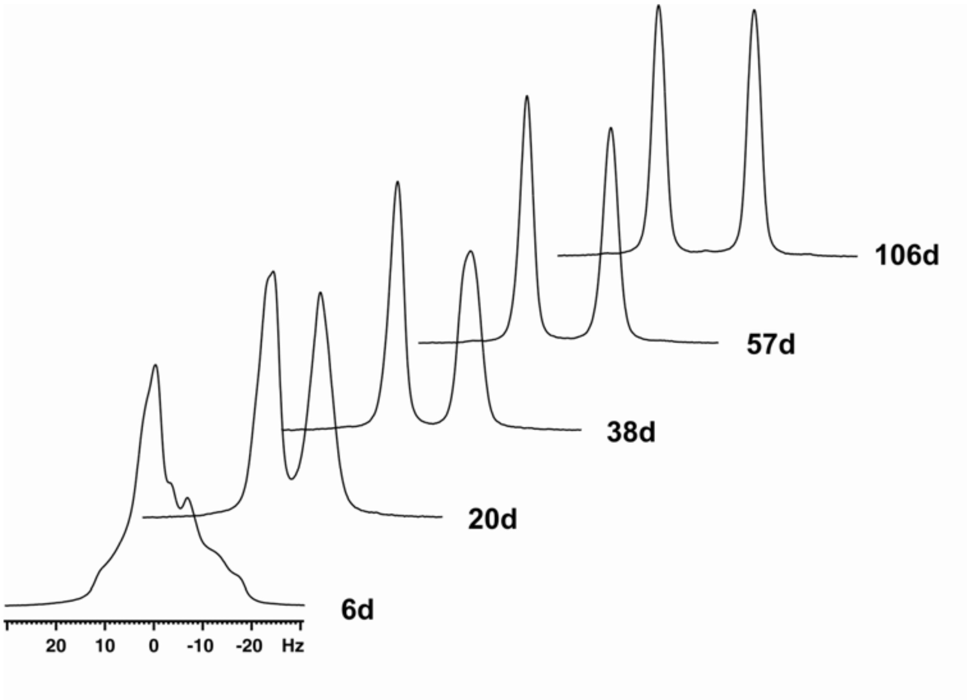


Figure S2. Equilibration of a PAN/DMSO-gel at room temperature in a silylated NMR-tube (irradiation dose = 320 kGy; final quadrupolar splitting $\Delta\nu_Q$=19.6 Hz) monitored by the ^{2}H-1D spectrum of DMSO-d$_6$.

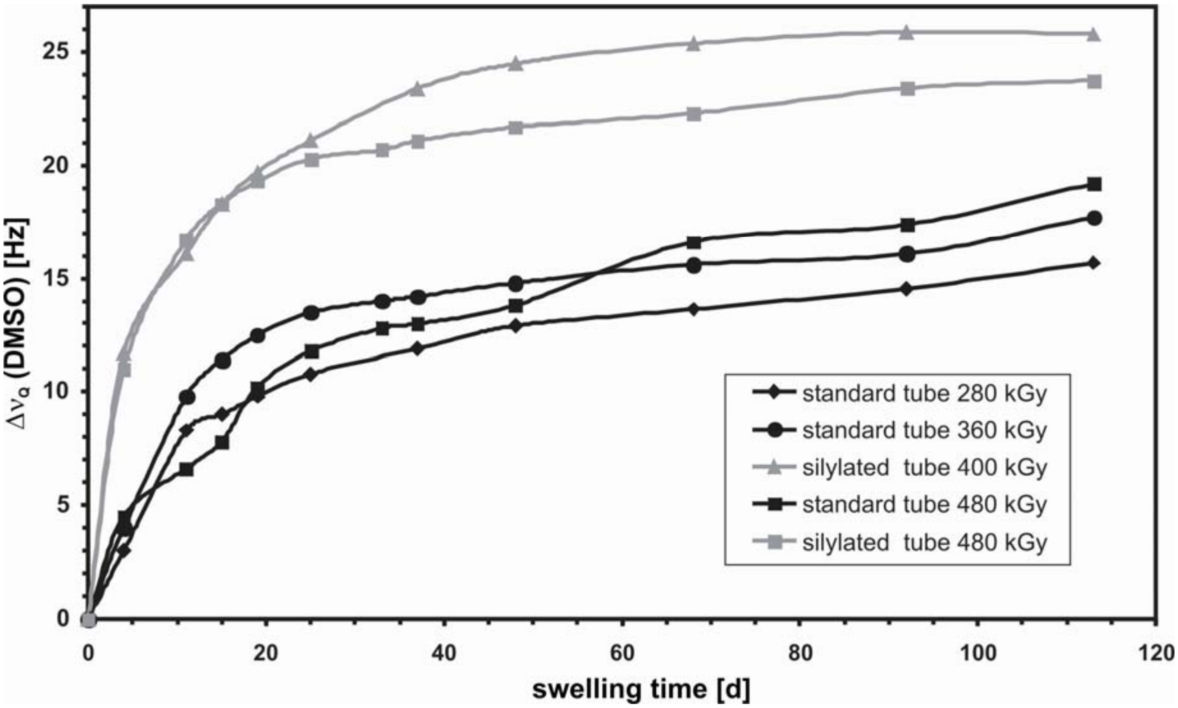


Figure S3. Quadrupolar splitting $\Delta\nu_Q$ of DMSO-d$_6$ taken from ^{2}H-1D spectra of five individual samples (MW=150000 g/mol) irradiated with 280 kGy, 360 kGy, and 480 kGy accelerated electrons in a conventional NMR-tube and 400 kGy and 480 kGy in NMR-tubes which were silylated prior to irradiation. Equilibration at room temperature is enhanced for silylated NMR-tubes.

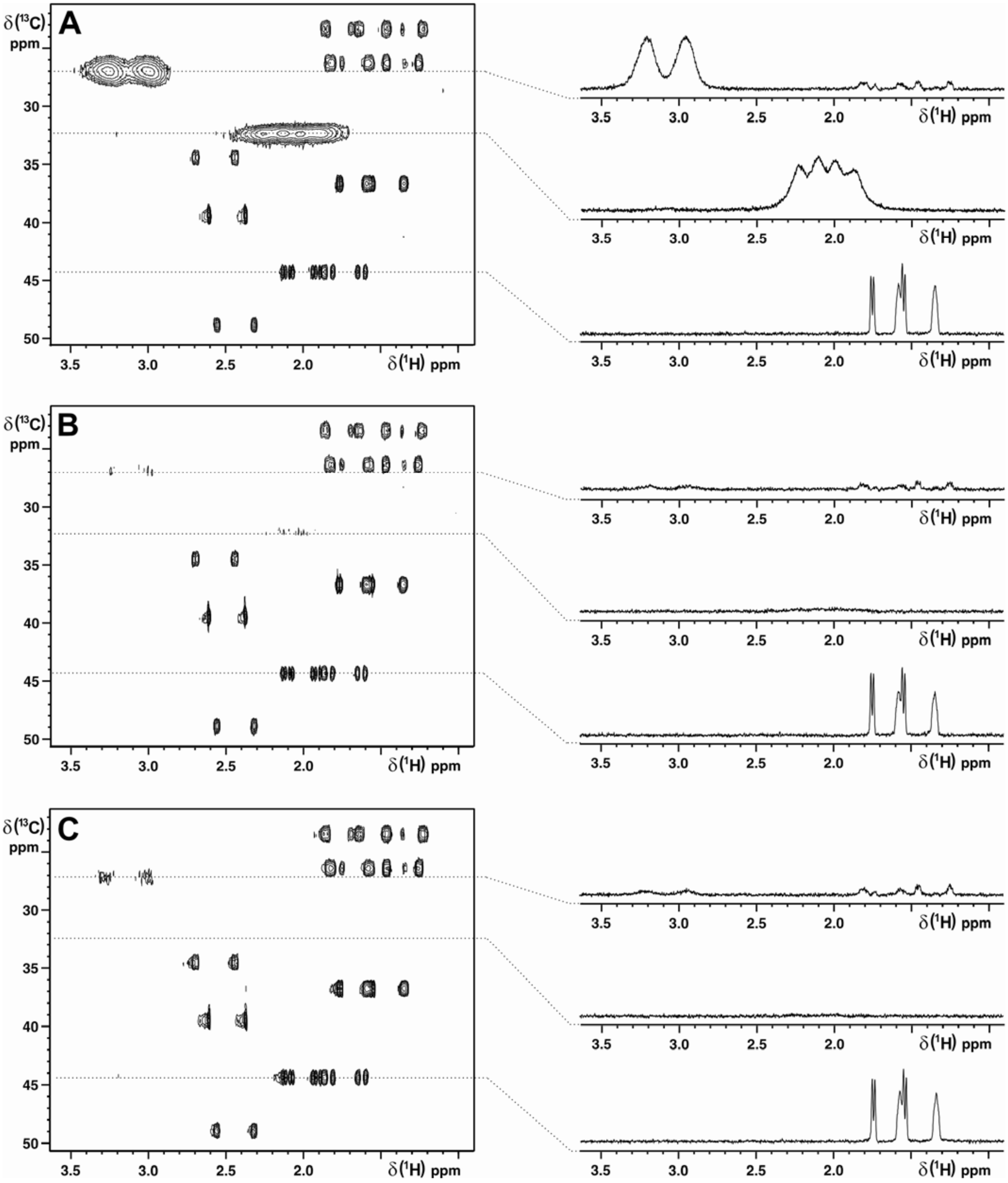
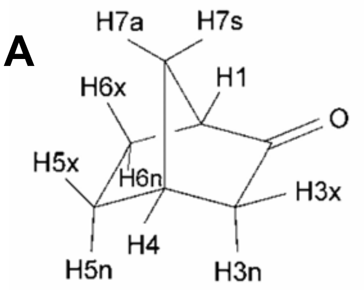


Figure S4. Suppression of polymer signals using CPMG and z-relaxation filters. (A) ^{1}H,^{13}C-HSQC without relaxation filter, (B) the same experiment with identical parameters with an additional 175 ms CPMG period[1] applied directly after the initial excitation pulse, (C) the experiment with a z-relaxation filter of 500 ms incorporated as described in [2]. Traces show the –CHCN– and –CH$_2$– groups of the polymer and the C3-H3x, C3-H3n cross peaks of ≈ 100 mM norcamphor for comparison. All traces and contours are scaled identical.

Table S1. Assignment and measured one-bond couplings for norcamphor in isotropic DMSO-solution and diffused into a PAN/DMSO-gel with a quadrupolar splitting $\Delta\nu_Q$ of 21.1 Hz.

Signal	$\delta(^{13}C)$ [ppm]	$\delta(^{1}H)$ [ppm]	$^{1}J_{CH}$ [Hz]	$^{1}J_{CH} + D_{CH}$ [Hz]	D_{CH} [Hz]
C1-H1	49.0	2.45	148.8 ± 0.2	145.4 ± 0.3	-3.4 ± 0.36
C3-H3x	44.4	2.01	128.1 ± 0.2	119.9 ± 0.5	-8.2 ± 0.54
C3-H3n		1.73	134.5 ± 0.3	128.6 ± 0.5	-5.9 ± 0.58
C7-H7s	36.8	1.67	133.5 ± 0.5	127.3 ± 0.5	-6.2 ± 0.71
C7-H7a		1.48	136.7 ± 0.5	143.6 ± 0.5	6.9 ± 0.71
C4-H4	36.8	2.57	144.8 ± 0.2	151.8 ± 0.3	7.0 ± 0.36
C5-H5x	34.6	1.71	131.9 ± 0.3	145.2 ± 1.0	13.3 ± 1.04
C5-H5n		1.48	133.2 ± 0.5	126.8 ± 0.3	-6.4 ± 0.58
C6-H6x	23.5	1.76	135.6 ± 0.3	130.7 ± 1.0	-4.9 ± 1.04
C6-H6n		1.35	134.1 ± 0.3	140.4 ± 0.7	6.3 ± 0.76

A



B

$D_a = 1.893447 \cdot 10^{-04}$
$D_r = 3.054770 \cdot 10^{-05}$
$A_{xx} = -1.4352 \cdot 10^{-04}$ (0.41650, -0.18779, 0.88953)
$A_{yy} = -2.3517 \cdot 10^{-04}$ (0.64699, 0.74860, -0.14489)
$A_{zz} = 3.7869 \cdot 10^{-04}$ (0.63869, -0.63587, -0.43329)
$R^2 = 0.998$

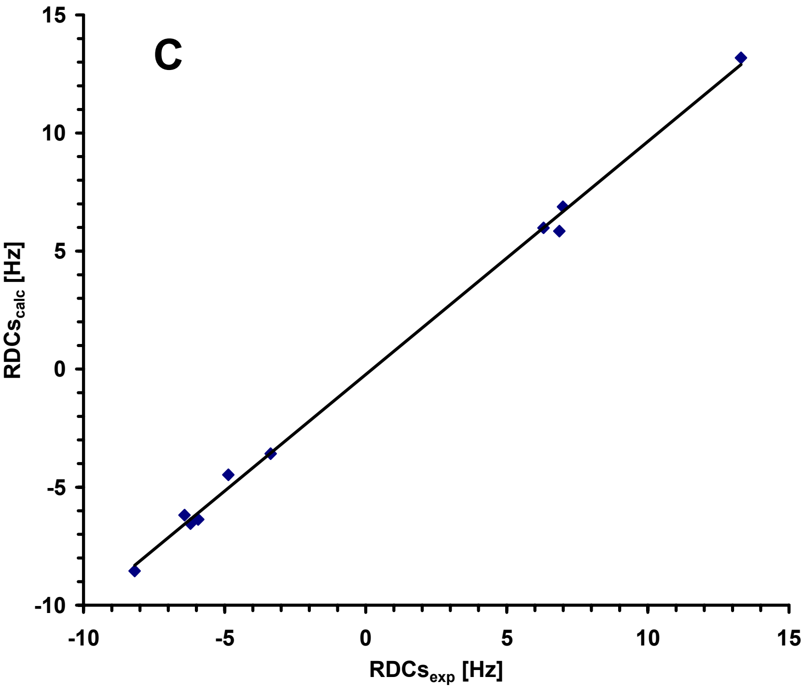


Figure S5. (A) Norcamphor. (B) Alignment tensor parameters and correlation factor R^2 of norcamphor as obtained by PALES[3] with the –bestFit option. (C) Experimental vs. fitted RDCs.

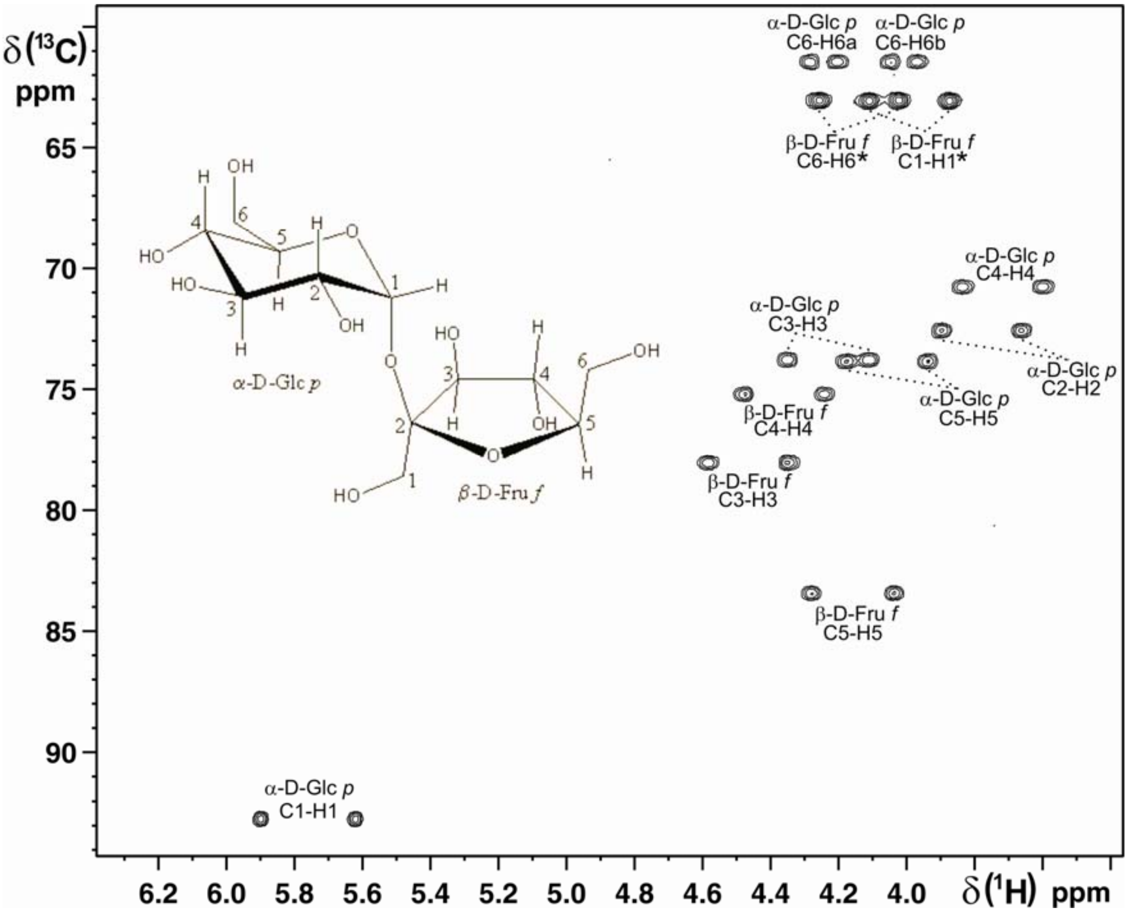


Figure S6. ^{1}H,^{13}C-HSQC of sucrose acquired inside a stretched PAN/DMSO-gel with a quadrupolar splitting $\Delta\nu_Q$ of DMSO-d_6 of 40.4 Hz. The structure of sucrose with corresponding numbering of the carbon atoms is shown as inlet.

Table S2. Measured one-bond couplings of sucrose in isotropic DMSO solution and diffused into a PAN/DMSO-gel with quadrupolar DMSO-d_6 deuterium splitting $\Delta\nu_Q$ of 40.4 Hz.

Signal	$^1J_{CH}$	$^1J_{CH}$+D_{CH}	D_{CH}
α-D-Glc*p* C6-H6a	141.1 ± 0.5 Hz	133.3 ± 0.8 Hz	-7.8 ± 0.9 Hz
α-D-Glc*p* C6-H6b	139.4 ± 0.5 Hz	151.5 ± 0.8 Hz	12.1 ± 0.9 Hz
(β-D-Fru*f* C6-H6*[a]	140.7 ± 1.0 Hz	135.5 ± 0.6 Hz	-5.2 ± 1.2 Hz)
(β-D-Fru*f* C1-H1*[a]	141.9 ± 0.3 Hz	144.9 ± 0.6 Hz	3.0 ± 0.7 Hz)
α-D-Glc*p* C4-H4	141.7 ± 0.4 Hz	146.1 ± 0.5 Hz	4.4 ± 0.6 Hz
α-D-Glc*p* C2-H2	141.1 ± 0.6 Hz	148.2 ± 0.3 Hz	7.1 ± 0.7 Hz
α-D-Glc*p* C3-H3	143.5 ± 0.7 Hz	150.0 ± 0.8 Hz	6.5 ± 1.1 Hz
α-D-Glc*p* C5-H5	143.3 ± 0.7 Hz	150.0 ± 0.8 Hz	6.7 ± 1.1 Hz
β-D-Fru*f* C4-H4	144.2 ± 1.0 Hz	128.8 ± 0.5 Hz	-15.4 ± 1.1 Hz
β-D-Fru*f* C3-H3	144.9 ± 1.0 Hz	126.2 ± 0.5 Hz	-18.7 ± 1.1 Hz
β-D-Fru*f* C5-H5	146.2 ± 0.6 Hz	128.4 ± 0.5 Hz	-17.8 ± 0.8 Hz
α-D-Glc*p* C1-H1	167.2 ± 0.4 Hz	182.5 ± 0.4 Hz	15.3 ± 0.6 Hz

[a] individual protons have not been resolved and measured RDCs can not be used for structural input

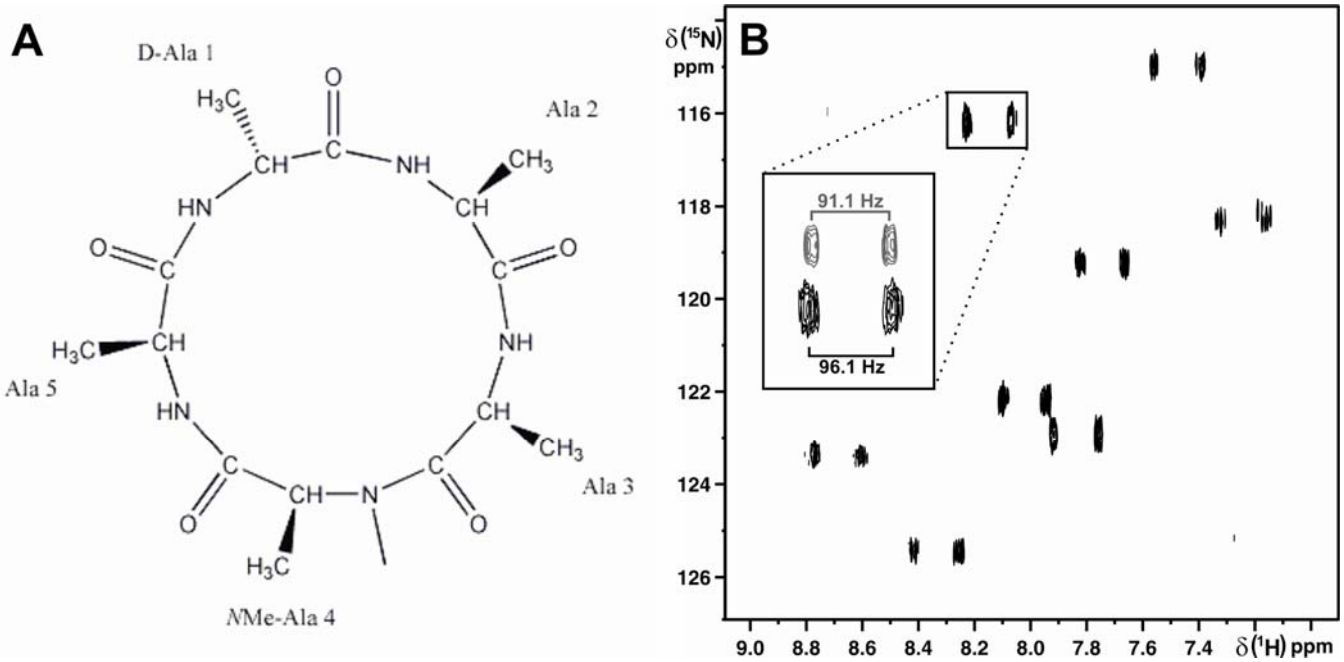


Figure S7. Structure (A) and coupled ^{1}H,^{15}N-HSQC (B) of the cyclic pentapeptide cyclo(-D-Ala-Ala-Ala-(*N*Me)Ala-Ala-) inside the PAN/DMSO-gel with $\Delta\nu_Q = 21.2$ Hz. The inlet compares the amide group of Ala 3 of conformer 1 with the cross peak in isotropic DMSO-d_6-solution (in gray).

Table S3. ^{1}H, ^{15}N and ^{13}C assignment for the two conformations of cyclo(-D-Ala-Ala-Ala-(*N*Me)Ala-Ala-). Isotropic chemical shift values are given in ppm.

	Hα	**Hβ**	**H$_{N\text{-Me}}$**	**HN**	**N**	**Cα**	**Cβ**	**CO**
conformer 1								
D-Ala 1	4.33	1.13	-	8.05	122.2	47.0	16.2	170.4
Ala 2	4.26	1.19	-	7.23	118.3	50.4	18.9	171.0
Ala 3	4.41	1.19	-	8.15	116.2	45.2	16.7	169.9
*N*Me-Ala 4	4.48	1.29	2.59	-	-	55.4	14.1	168.5
Ala 5	4.37	1.18	-	7.81	122.9	47.1	16.5	170.1
conformer 2								
D-Ala 1	4.10	1.16	-	8.38	125.5	49.2	16.4	172.5
Ala 2	3.93	1.27	-	8.68	123.4	49.6	16.6	171.1
Ala 3	4.61	1.09	-	7.48	115.0	45.1	17.7	171.5
*N*Me-Ala 4	3.52	1.54	2.85	-	-	64.6	14.8	171.6
Ala 5	4.45	1.17	-	7.74	119.1	47.1	16.0	169.9

Table S4. One-bond couplings measured for conformer 1 of the pentapeptide cyclo(-D-Ala-Ala-Ala-(*N*Me)Ala-Ala-) in isotropic DMSO-d_6 solution and inside the PAN/DMSO-d_6 gel with $\Delta\nu_Q$ = 21.2 Hz.

Signal		**$^1J_{XH}$ [Hz]**	**$^1J_{XH}$+D_{XH} [Hz]**	**D_{XH} [Hz]**
D-Ala 1	Cβ-Hβ	128.3 ± 0.1	128.7 ± 0.3	0.4 ± 0.3
D-Ala 1	Cα-Hα	136.6 ± 0.3	142.3 ± 2.0	5.7 ± 2.0
D-Ala 1	N-NH	91.2 ± 0.3	94.6 ± 2.5	3.4 ± 2.5
Ala 2	Cβ-Hβ	128.5 ± 0.1	127.8 ± 0.5	-0.8 ± 0.5
Ala 2	Cα-Hα	143.3 ± 0.2	157.8 ± 2.5	14.5 ± 2.5
Ala 2	N-NH	91.0 ± 0.7	95.8 ± 1.5	4.8 ± 1.7
Ala 3	Cβ-Hβ	128.7 ± 0.2	130.7 ± 0.6	2.0 ± 0.6
Ala 3	Cα-Hα	138.2 ± 0.3	150.6 ± 2.0	12.4 ± 2.0
Ala 3	N-NH	91.1 ± 0.2	96.1 ± 1.5	5.0 ± 1.5
*N*Me-Ala 4	Cβ-Hβ	128.5 ± 0.2	130.3 ± 0.6	1.8 ± 0.6
*N*Me-Ala 4	Cα-Hα	134.9 ± 0.4	142.3 ± 2.0	7.4 ± 2.0
*N*Me-Ala 4	Cm-Hm	138.8 ± 0.1	136.0 ± 0.8	-2.8 ± 0.8
Ala 5	Cβ-Hβ	128.1 ± 0.1	123.6 ± 0.5	-4.5 ± 0.5
Ala 5	Cα-Hα	136.5 ± 0.5	142.5 ± 3.5	6.0 ± 3.5
Ala 5	N-NH	91.5 ± 0.2	95.1 ± 1.5	3.6 ± 1.5

Table S5. One-bond couplings measured for conformer 2 of the pentapeptide cyclo(-D-Ala-Ala-Ala-(*N*Me)Ala-Ala-) in isotropic DMSO-d_6 solution and inside the PAN/DMSO-d_6 gel with $\Delta\nu_Q$ = 21.2 Hz.

Signal		**$^1J_{XH}$ [Hz]**	**$^1J_{XH}$+D_{XH} [Hz]**	**D_{XH} [Hz]**
D-Ala 1	Cβ-Hβ	128.3 ± 0.1	122.8 ± 2.0	-5.5 ± 2.0
D-Ala 1	Cα-Hα	142.8 ± 0.4	165.6 ± 1.0	22.8 ± 1.1
D-Ala 1	N-NH	92.8 ± 0.3	98.2 ± 1.5	5.4 ± 1.5
Ala 2	Cβ-Hβ	129.1 ± 0.1	136.4 ± 1.3	7.3 ± 1.3
Ala 2	Cα-Hα	143.5 ± 0.3	171.3 ± 3.0	27.8 ± 3.0
Ala 2	N-NH	92.4 ± 8.0	104.5 ± 5.0	12.1 ± 9.4
Ala 3	Cβ-Hβ	128.5 ± 0.2	128.4 ± 0.6	-0.1 ± 0.6
Ala 3	Cα-Hα	139.3 ± 0.3	175.7 ± 1.5	36.4 ± 1.5
Ala 3	N-NH	91.6 ± 0.3	102.2 ± 5.0	10.6 ± 5.0
*N*Me-Ala 4	Cβ-Hβ	129.0 ± 0.1	123.6 ± 0.5	-5.4 ± 0.5
*N*Me-Ala 4	Cα-Hα	139.8 ± 0.8	159.3 ± 4.0	19.5 ± 4.1
*N*Me-Ala 4	Cm-Hm	138.8 ± 0.1	131.3 ± 1.0	-7.5 ± 1.0
Ala 5	Cβ-Hβ	128.7 ± 0.1	130.3 ± 1.0	1.6 ± 1.0
Ala 5	Cα-Hα	141.4 ± 0.5	158.4 ± 5.0	17.0 ± 5.0
Ala 5	N-NH	89.7 ± 0.5	94.04 ± 3.0	4.3 ± 3.0

Gel preparation:

Non-cross-linked polymers:

Two kinds of linear poly(acrylonitrile) were used:

1. Poly(acrylonitrile) purchased by *Polyscience, Inc.* (MW=150000 g/mol)

2. Poly(acrylonitrile) polymerized in-house by precipitation polymerization in water with the redox system $K_2S_2O_8/K_2S_2O_5$ as radical initiator ($M_{n,osm}$=231000 g/mol).

Precipitation of PAN-sticks:

Sticks of poly(acrylonitrile) were obtained by precipitation out of a dimethylsulfoxide solution: A highly viscous solution of PAN in DMSO (≈ 300 g/L) was filled in paper rolls with inner diameters of 3.5-4.5 mm. The filled paper rolls were then placed in solutions with stepwise increased content of methanol: 1. DMSO/MeOH 2:1 (20 min, 80°C), 2. DMSO/MeOH 1:1 (20 min, 65°C), 3. pure MeOH (1 h, 50°C). Finally, the paper was removed and precipitated PAN-sticks were dried at 70°C for 24 h. By this procedure PAN-sticks of 2.5-3.5 mm were obtained.

PAN/DMSO-d_6-solutions for irradiation:

PAN/DMSO-d_6-solutions with concentrations of 140 g/L, 210 g/L and 280 g/L were filled in standard 5mm-NMR-tubes and in silylated NMR-tubes. Tubes were silylated by treatment with a 1:1 mixture of $ClSi(CH_3)_3$ and $Cl_2Si(CH_3)_2$ for 24 h at room temperature and washed 3 times with dichloromethane before drying.

Cross-linking by irradiation:

PAN-sticks and PAN/DMSO-d_6-solutions were irradiated with 10 MeV electrons generated by an industrial electron accelerator (*Beta-Gamma-Systems* in Saal an der Donau, Germany). Sticks and tubes were placed perpendicular to the electron beam during irradiation.

The samples were irradiated by single irradiation doses of 40 kGy which took several seconds each. The time interval between two subsequent irradiation steps was approximately 10-15 min. Total irradiation doses of 120-480 kGy were applied.

References

(1) Carr, H. Y.; Purcell, E. M. *Phys. Rev.* **1954**, *94*, 630.

(2) Luy, B.; Kobzar, K.; Knör, S.; Furrer, J.; Heckmann, D.; Kessler, H. *J. Am. Chem. Soc.* **2005**, *127*, 6459-6465.

(3) Zweckstetter, M.; Bax, A. *J. Am. Chem. Soc.* **2000**, *122*, 3791-3792.