Supplementary Material (ESI) for Chemical Communications

Supporting Information

Artifact-Free Measurement of Residual Dipolar Couplings in DMSO by the Use of Cross-Linked Perdeuterated Poly(acrylonitrile) as Alignment Medium

Grit Kummerlöwe,[a,c] Marc Behl,[b] Andreas Lendlein[b] and Burkhard Luy[a,d]*

[a] *Department Chemie, LS OC II, Technische Universität München, Lichtenbergstr. 4, 85747 Garching, Germany. Fax:+49 89 289 13210; Tel: +49 89 289 13275; E-mail: Burkhard.Luy@kit.edu*

[b] *Center for Biomaterial Development, Institute of Polymer Research, GKSS Research Center GmbH, Kantstr. 55, 14513 Teltow, Germany.*

[c] *Current address:Institut für Biologische Grenzflächen, Karlsruher Institut für Technologie, Herrmann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.*

[d] *Current address:Institut für Organische Chemie, Karlsruher Institut für Technologie, Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany.*

E-mail: Burkhard.Luy@kit.edu

Data concerning the 11-mer peptide

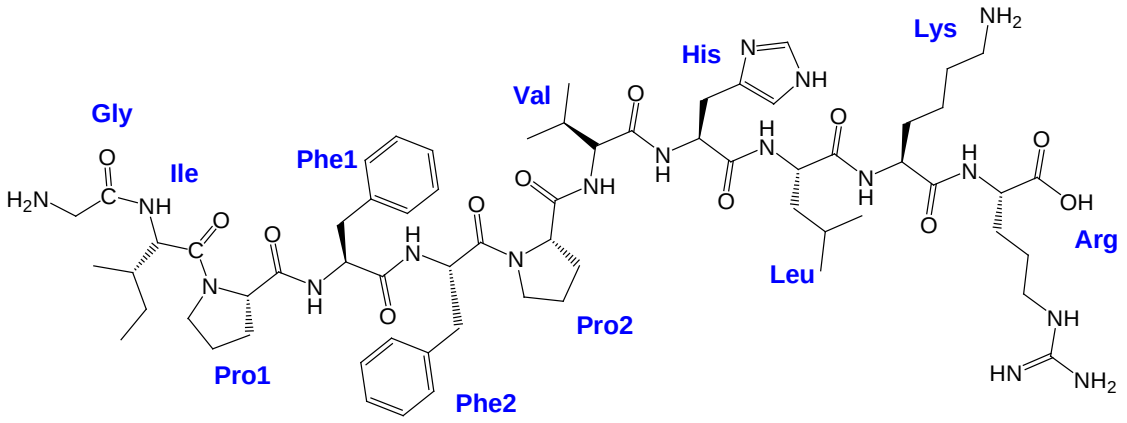

Figure S1. Linear 11-mer peptide derived from SPC(FFI) used for demonstration of dPAN/DMSO-d_6 gels as alignment medium.

Table S1: One-bond proton carbon couplings measured for the peptide shown in Figure S1. Residual dipolar couplings (D_{CH}) are calculated from the difference of couplings measured in a stretched dPAN/DMSO gel ($^1J_{CH} + D_{CH}$) and in DMSO solution ($^1J_{CH}$).

Signal	$^1J_{CH}$ [Hz]	$^1J_{CH} + D_{CH}$ [Hz]	D_{CH} [Hz]
Ile Cδ - Hδ	124.9 ± 0.1	123.3 ± 0.2	-1.6 ± 0.2
Ile Cγ' - Hγ'	125.9 ± 0.1	127.4 ± 0.2	1.5 ± 0.2
Leu Cδ2 - Hδ2	125.6 ± 0.2	125.6 ± 0.4	0.0 ± 0.4
Leu Cδ1 - Hδ1	125.9 ± 0.1	128.8 ± 0.3	2.9 ± 0.3
His Cβ - Hβ1	132.8 ± 0.4	140.0 ± 2.0	7.2 ± 2.0
His Cβ - Hβ2	131.4 ± 0.4	127.3 ± 3.0	-4.1 ± 3.0
Val Cβ - Hβ	130.1 ± 0.3	130.0 ± 0.4	-0.1 ± 0.5
Arg Cβ- Hβ1	127.4 ± 0.5	136.3 ± 0.5	8.9 ± 0.7
Arg Cβ - Hβ2	129.9 ± 0.5	124.3 ± 0.5	-5.6 ± 0.7
Ile Cβ - Hβ	129.3 ± 0.3	135.3 ± 0.5	6.0 ± 0.6
Pro2 Cδ - Hδ1	144.4 ± 0.3	159.1 ± 2.0	14.7 ± 2.0
Pro2 Cδ - Hδ2	145.0 ± 0.3	130.9 ± 3.0	-14.1 ± 3.0
Pro1 Cδ - Hδ1	145.2 ± 0.3	150.8 ± 2.0	5.6 ± 2.0
Pro1 Cδ - Hδ2	142.8 ± 0.3	128.7 ± 3.0	-14.1 ± 3.0
Lys Cα - Hα	140.6 ± 0.2	153.5 ± 0.4	12.9 ± 0.4
Phe2 Cα - Hα	140.5 ± 0.3	155.7 ± 0.8	15.2 ± 0.9
Arg Cα - Hα	139.8 ± 0.2	157.4 ± 0.5	17.6 ± 0.5
Phe1 Cα - Hα	141.7 ± 0.2	156.3 ± 0.8	14.6 ± 0.8
Ile Cα - Hα	138.7 ± 0.2	147.6 ± 0.6	8.9 ± 0.6
Val Cα - Hα	140.3 ± 0.2	154.8 ± 0.8	14.5 ± 0.8
Pro1 Cα - Hα	146.7 ± 0.3	156.5 ± 0.6	9.8 ± 0.7
Pro2 Cα - Hα	146.5 ± 0.3	159.3 ± 1.5	12.8 ± 1.5

Determination of molecular weights of poly(acrylonitrile-d_3) (dPAN)

Molecular weights of poly(acrylonitrile-d_3) prior cross-linking were determined on a multidetector GPC, which consisted of a GRAM VS1 precolumn (40 mm x 4.6 mm), a GRAM 30A5091312 and a GRAM 10*3 71111 column (both 250 mm x 4.6 mm) (all *PSS*, Mainz, Germany), a CO=200 column oven (*W.O. electronics*, Langenzerdorf, Germany), an isocratic pump 980, an automatic injector 851-AS, a LG 980-02 ternary gradient unit, a multiwave length detector MD-910, a RI detector RI-930 (all *Jasco*, Groß-Umstadt, Germany), a differential viscometer η-1001 (*WGE Dr. Bures*, Dallgow-Doeberitz, Germany), a Wyatt miniDawn Tristar light scattering detector (*Wyatt Technology Corporation*, Santa Barbara, USA), a degasser ERC-3315α (*Ercatech AG*, Berne, Switzerland), and dimethylformamide (0.4 wt% toluene as internal standard, 35 °C, 1.0 mL·min^{-1}) as eluent by universal calibration with polystyrene standards using WINGPC 6.2 (*PSS*) software.

Cross-linking of poly(acrylontrile-d_3) (dPAN)

A dPAN/DMSO-d_6-solution with a concentration of 220 g/L was filled in glass and Teflon® tubes of 2.4; 3,0; and 3;4 mm inner diameter. Polymer solutions were irradiated with 10 MeV electrons generated by an industrial electron accelerator (Beta-Gamma-Systems, Saal an der Donau, Germany). During irradiation, tubes were placed perpendicular to the electron beam.

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.

Cross-linking of poly(acrylonitrile) (PAN)

Cross-linked PAN was prepared in an analogues procedure and as described previously[1] using linear non-deuterated PAN (M_w = 150000 g/mol).

Characterization of cross-linked poly(acrylontriles)

The obtained e-beam irradiated samples were dried in a vacuum oven at 80 °C until constant weight was achieved. A gel content (G) above 94% was obtained for the PAN samples. The volume based degree of swelling (S) decreased with increasing total irradiation doses, attributed to an increase in cross-linking density. This increase in cross-linking density could be confirmed by the calculation of the polymer chain segment length (M_c) between two netpoints, according to the affine and the phantom network model, using equations (1) and (2) (see Table S2). The phantom model is supposed to give a better correlation with experimentally determined values. In case of the cross-linked dPAN sample *G* decreased to 86%, which can be speculated to result from the lower M_w of the dPAN, an electron shielding of the Teflon® tube, as well as an inherent shielding from the deuterium atoms in the dPAN compared the hydrogen atoms in the PAN. Consequently, for the dPAN sample a higher *S* as well as a higher M_c compared to the PAN sample with the same total irradiation dose was obtained.

$$M_c = \frac{\rho_p \cdot V_s \cdot \left(A \cdot \upsilon_p^{1/3} - B \cdot \upsilon_p\right)}{\ln\left(1-\upsilon_p\right) + \upsilon_p + \chi \cdot \upsilon_p^{2}} \qquad (1)$$

V_s: molar volume DMSO = 71.02 $L \cdot mol^{-1}$; $v_p = 1/S$
χ Flory-Huggins interaction parameter, calculated according equation (2)

$$\chi \approx 0.34 + \frac{V_s}{R \cdot T} \cdot \left(\delta_s - \delta_p\right)^2 \qquad (2)$$

V_s: molar volume (DMSO, 71.02 $L \cdot mol^{-1}$); δ_s solubility parameter of solvent (DMSO, 29.07 $(MPa)^{1/2}$); δ_p solubility parameter of polymer (PAN, 26.09 $(MPa)^{1/2}$), value of PAN was used in case of dPAN

Table S2: *G* gel content, *S* volume based degree of swelling, ρ_p density of nonswollen polymer, $M_{c,phantom}$ polymer chain segment length between two netpoints according to the affine polymer network model, $M_{c,phantom}$ polymer chain segment length between two netpoints according to the phantom network model

Sample-ID[a]	G[b] **[%]**	S[b] **[%]**	ρ_p[c] **[g·mL^{-1}]**	$M_{c,affine}$[d] **[g·mol^{-1}]**	$M_{c,phantom}$[d] **[g·mol^{-1}]**
PAN240	94.3 ± 1.0	4020 ± 60	1.0913	165.400 ± 3.900	86.400 ± 2.000
PAN320	96.2 ± 0.8	3100 ± 60	1.0916	107.700 ± 3.400	56.700 ± 1.800
PAN480	95.5 ± 2.5	2120 ± 130	1.0945	58.100 ± 5.600	31.100 ± 2.900
dPAN480	86.2 ± 3.5	2700 ± 140	1.1422	89.000 ± 7.700	47.000 ± 4.000

[a] denoted as XY with X representing the cross-linked polymer (PAN or dPAN), and Y the radiation dose in kGy
[b] determined in DMSO
[c] determined with a Micro-Ultrapycnometer 1000 (*Quantachrome Instruments*, Boynton Beach, USA)
[d] determined using equations (1) and (2), affine model $A = 1$, $B = 2/f$, phantom model $A = (f-2)/f$, $B = 0$; A structure factor, B volume factor, f functionality of the crosslinks ($f = 4$). A functionality of 4 for the cross-links has been selected as in the investigation of the cross-linking PAN by γ-radiation a cross-linking via reaction of two nitrogen atoms of the nitrile groups was demonstrated.[2]

References

[1] G. Kummerlöwe, J. Auernheimer, A. Lendlein and B. Luy, *J. Am. Chem. Soc.*, 2007, **129**, 6080-6081.
[2] S. M. Badawy and A. M. Dessouki, *J. Phys. Chem. B*, 2003, **107**, 11273-11279.