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NMR Spectroscopy

Polyacetylenes as Enantiodifferentiating Alignment Media**

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The availability of residual dipolar couplings (RDCs) measured in weakly aligned media has had a major impact on the structural characterization of dissolved (chiral) molecules by NMR spectroscopy.[1] This has been and still is especially true for biomacromolecules[2] but more recently, the field has seen a rapidly increasing interest in the application of RDCs to solve structural problems for small molecules, too.[1e,3] This, at first sight surprising fact, is by no means a back-extension, because the molecules under investigation pose problems being absent in the above-mentioned biopolymers. In contradiction to the latter many small molecules contain stereogenic units of unknown relative and absolute configuration. Given the fact that configurational analysis is always a problem of conformational analysis at the same time, the simultaneous treatment of both structural aspects is a necessity to solve the stereochemical problem exhaustively.[4]

With the advent of RDCs as a new NMR parameter containing distance and angle information the scope of NMR-based stereochemical analysis has been broadened considerably. This is mainly because of the fact that RDCs deliver conformationally relevant information without the need for parametrization as is the case for the evaluation of scalar couplings.[5] Moreover, RDCs are global parameters not relying on short-range interactions like cross-relaxation (nuclear Overhauser effect, NOE)[6] or cross-correlated relaxation.[7]

A precondition for the measurement of RDCs, as anisotropic NMR parameters, is to partially orient the analyte with respect to the magnetic field (weak alignment: RDC amounts approximately 10^{-3} of the maximum dipolar coupling). This can be done either by stretched polymer gels (SAG = strain-induced alignment in a gel) or by dissolving the compound in a lyotropic liquid-crystalline (LLC) phase.[3a,b,l] In the last years considerable progress has been made in the field of these orienting or alignment media especially for typical organic molecules being insoluble in water. On the other hand if the determination of the absolute configuration of a chiral, nonracemic water-insoluble compound is the goal of the investigation, it is necessary to orient the analyte in an enantiodifferentiating manner. This in turn is possible only if the alignment medium is itself chiral and of uniform configuration. The number of media fulfilling these criteria is still extraordinary small.[1e] As far as chiral LLC phases are concerned, only the homopolypeptide-based LLC phases derived from poly-γ-benzyl-L/D-glutamate (PBLG/PBDG), poly-γ-ethyl-L-glutamate (PELG/PEDG), and poly-ε-carboxybenzoyl-L/D-lysin (PCBLL/PCBDL)[8] as well as a recently introduced polyguanidine[9] are known to meet the described needs. Moreover, Luy and co-workers have shown that gelatin cross-linked by accelerated electrons (e$^-$-gelatin) allows for the distinction of enantiomers in DMSO and DMSO/D_2O mixtures at temperatures up to 60 °C.[10]

Despite our encouraging results with the polyguanidines,[9] we decided to look for alternative helically chiral polymers capable of forming LLC phases. This decision was driven by a number of drawbacks associated with the polyguanidines. First of all the linewidths of the NMR signals from the analyte are rather large which hampers a precise determination of RDCs. Furthermore, the induced alignment is too strong which may lead to strong coupling artifacts. Finally, the purification of the noncrystalline carbodiimide monomers suffers from decomposition during chromatography.

Within the family of helically chiral polymers[11,12] the amino-acid-stabilized polyisocyanides[13] and polyacetylenes[14] look most promising. Both polymer types are known to form LLC phases[13c,d,14f,g,h] in a number of organic solvents and they are characterized by large persistence lengths[13d,14h] (depending on the solvent) which should reduce the critical concentration for the phase transition.[15] Moreover, the synthesis of the corresponding monomers is straightforward and their transition-metal-induced polymerization works efficiently with a high tolerance for functional groups.[14e,16] In this contribution we would like to describe the suitability of the valine-derived polyacetylene **p1** and its enantiomer **p2** as alignment media.

The synthesis of monomer **1** was achieved in three steps starting from 4-iodobenzoic acid ethyl ester **2** and valine **3** (Scheme 1; for a detailed description see the Supporting Information).[17]

According to the work of Okoshi and Yashima[14f,18] the polymerization of **1** was initiated by $[Rh(nbd)Cl]_2$ delivering polymer **p1** as a yellow solid (nbd = norbornadiene). This polymerization reaction was repeated three times whereby a total of four different polymer samples (**p1a**, **p1b**, **p1c**, and

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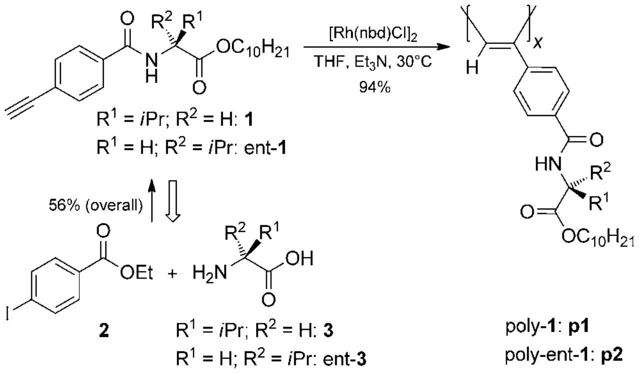
Supporting information for this article, including experimental details for the monomer, polymer, the phase preparations, and the sample compositions as well as the definitions of the tensor comparison sets and the tensor calculations, is available on the WWW under http://dx.doi.org/10.1002/anie.201201891.



Scheme 1. Synthesis and polymerization of monomer **1**.

p1d) were obtained (see Table SI1 in the Supporting Information). The polymerization of ent-**1** delivered polymer **p2** (two preparations: **p2a**, **p2b**) which is not exactly the enantiomer of **p1** (different molecular weight, different polydispersity) but can be treated as such to a good approximation. Since it is known from the literature that the polymerization of monosubstituted acetylenes by rhodium complexes yield cis–transoidal backbone conformations,[19] we expect this to be the case for **p1** and **p2**, too. Moreover, the polymers exhibit a strong induced circular dichroism related to the π–π* transitions of the conjugated backbone indicating their preferred one-handed helical structure (see Figures SI1 to SI6 in the Supporting Information). As expected, the circular dichroism (CD) spectra of the different **p1** preparations closely resemble those spectra of the L-alanine-derived polymer investigated by Yashima et al.[14f,h,i] and the L-valine-derived octyl ester studied by Tang et al.[20] From AFM studies of the former[21] it was deduced that this polymer forms right-handed helices in chloroform solutions which, together with the CD data, entails that this is also true for **p1a–d**. Interestingly, because of a slight modification of the preparation procedure, **p1a** and **p1d** differ from the other two **p1** polymer samples with respect to molecular weight and polydispersity (see Table SI1 in the Supporting Information). Since **p1a** displayed the highest molecular weight, we started our investigations with this polymer.[8l]

As expected from the work of Yashima[14f] **p1a** forms a LLC phase starting at about 18% (w/w) in chloroform. The phase transition was monitored by observing the quadrupolar splitting of the deuterium signal of the deuterated solvent accompanied by the disappearance of the isotropic signal. All **p1** and **p2** preparations showed this behavior. Moreover, they are chiral and of uniform configuration. The latter property should allow for their application to differentiate enantiomers of chiral analytes and, as a final goal, the determination of their absolute configuration. To evaluate the enantiodifferentiating properties of **p1** we performed a series of experiments with both enantiomers of isopinocampheol ((+)- and (−)-IPC). This choice is based on the fact that this alcohol is available in both enantiomeric forms and on the existence of two other studies probing the enantiodifferentiating properties of chiral LLC phases with this compound.[9,22]

To learn as much as possible about the orienting properties of the new polymers we prepared 13 anisotropic samples of IPC in the polymer preparations **p1a–p1c** and **p2a** (**p1d** and **p2b** have been used to demonstrate the differentiation of enantiomers with strychnine, Figure 2b).[29] Moreover, for comparison we recalculated the alignment tensors for the IPC enantiomers in PBLG using data from the literature.[22] For all samples RDCs ($^1D_{\mathrm{CH}}$) were extracted from CLIP-HSQC[23] spectra (see Table 1 for four representative data sets; for experimental details and all other data sets see the Supporting Information). As illustrated in Figure 1 the peaks are pleasantly narrow, even in comparison to PBLG of high molecular weight.[8l]

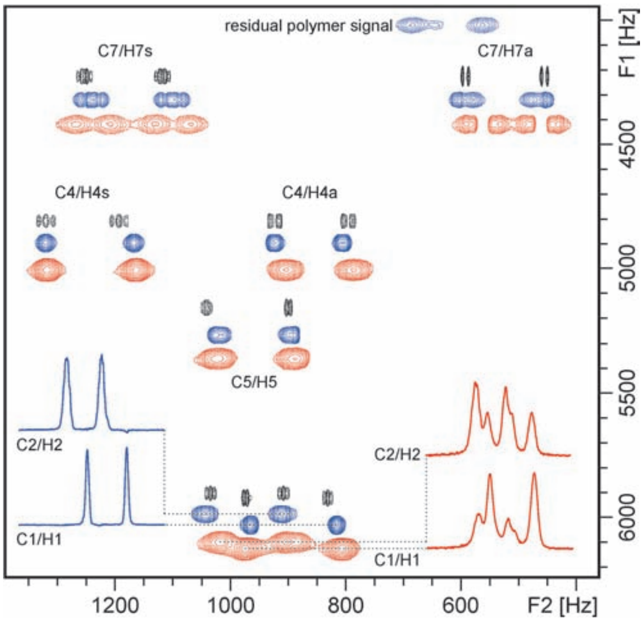
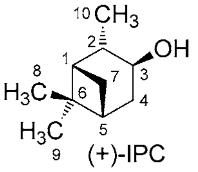
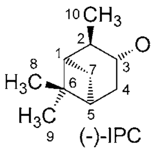


Figure 1. Parts of 500 MHz ^{1}H,^{13}C-CLIP-HSQC spectra of (+)-IPC in isotropic phase (CDCl$_3$, black contours), in 20% (w/w) **p1a** (anisotropic, blue contours) and in 8.1% (w/w) PBLG (anisotropic, red contours). The inserted traces from the 2D spectra (C1/H1 and C2/H2) illustrate the favorable line widths achieved with **p1a** (F1 = carbon frequency and F2 = hydrogen frequency).

Furthermore, the RDCs cover a favorable range of about −10 to +15 Hz which allows for their precise measurement without notable irritations by strong coupling artifacts. To our delight the couplings from the two enantiomers of IPC are different, which means that their respective orientations in the chiral polyacetylenes are different, too (see Table 1, Figure 2a, and the Supporting Information). To quantify these differences, we calculated the alignment tensors for both enantiomers in **p1a–c** and **p2a** (13 tensors) using a SVD-based[24] (SVD = singular value decomposition) modified version of the program hotFCHT).[3f,25] Together with the two tensors from the PBLG samples a total of 15 tensors (8 tensors from samples containing (+)-IPC and 7 tensors from samples containing (−)-IPC) were obtained. 49 out of the 105 possible tensor comparisons were grouped into 11 tensor comparison sets (Figure 3 and Tables SI3 and SI4 in the Supporting Information).

Table 1: Chemical shifts (δ_C and δ_H) and coupling constants (*J* and *D*) of (+)- and (−)-IPC in isotropic and anisotropic phases at 300 K.





Isotropic sample					Anisotropic samples[a]			
					(+)-IPC		(−)-IPC	
C	δ_C [ppm]	H	δ_H [ppm]	$^1J_{CH}$ [Hz]	$^1D_{CH}$ ($^1D_{CC}$) [Hz][c,f] **p1a-7**	$^1D_{CH}$ ($^1D_{CC}$) [Hz][b,f] **p1b-19**	$^1D_{CH}$ ($^1D_{CC}$) [Hz][d,f] **p1b-7***	$^1D_{CH}$ ($^1D_{CC}$) [Hz][e,f] **p1a-5**
1	47.83	1	1.79	139.5	4.4	9.0	−20.8	−9.0
2	47.69	2	1.93	125.8	3.4	1.9	12.5	5.4
3	71.59	3	4.06	139.6	8.5	6.4	9.9	13.9
4	39.03	4s	2.51	126.0	14.7	13.1	−3.3	3.7
4	39.03	4a	1.71	126.0	−4.2	−4.1	4.5	1.7
5	41.77	5	1.93	143.7	−7.7	−16.5	−9.3	−5.1
6	38.16	–	–	–	–	–	–	–
7	34.37	7s	2.37	135.4	1.7	7.8	8.6	5.0
7	34.37	7a	1.04	136.0	−5.9	−3.6	13.8	−1.3
8	27.68	8	1.21	123.0	2.2 (−0.6)	0.2 (−0.1)	−2.1 (0.6)	1.7 (−0.5)
9	23.70	9	0.91	124.6	−3.0 (0.81)	−3.0 (0.8)	−3.8 (1.1)	−4.3 (1.2)
10	20.74	10	1.13	124.4	1.5 (−0.41)	3.7 (−1.0)	1.7 (−0.5)	−0.7 (0.2)

[a] For the sample composition see Table SI2 in the Supporting Information. [b] $\Delta\nu Q = 76.7$ Hz. [c] $\Delta\nu Q = 30.1$ Hz. [d] $\Delta\nu Q = 67.8$ Hz. [e] $\Delta\nu Q = 29.2$ Hz. [f] The values in brackets are $^1D_{CC}$ couplings calculated from the measured $^1D_{CH_3}$ couplings according to Ref. [28].

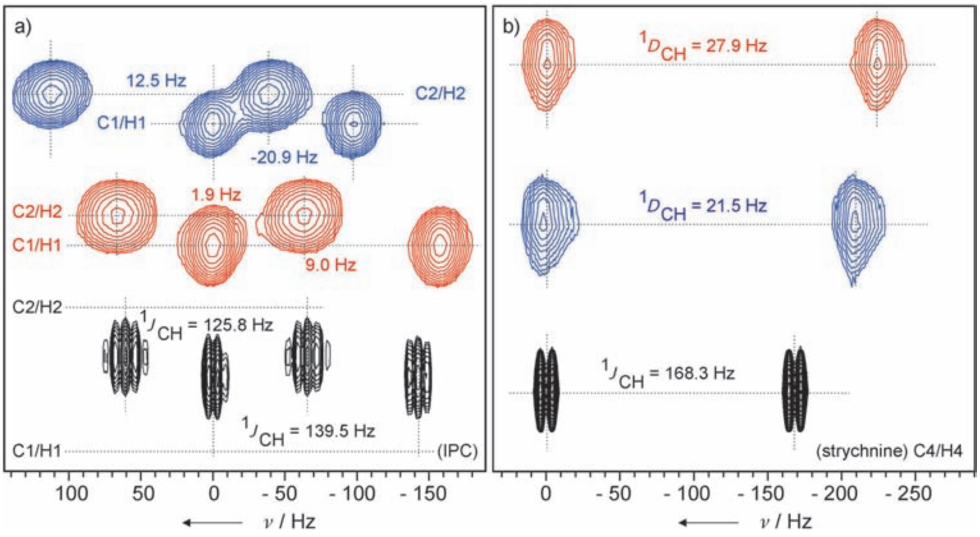


Figure 2. Parts of 500 MHz ^{1}H,^{13}C-CLIP-HSQC spectra. a) (+)-IPC in isotropic phase (CDCl$_3$, black contours), (−)-IPC in **p1b-7*** (anisotropic, blue contours) and (+)-IPC in **p1b-19** (anisotropic, red contours).
b) Strychnine: isotropic (black), anisotropic in **p2b-6** (blue), and anisotropic in **p1d-4** (red). For the exact compositions of the samples see Table SI2 in the Supporting Information (*J* = isotropic coupling constant and *D* = residual dipolar coupling).

The comparison of four tensor pairs, calculated from IPC samples in **p1a**, pairwise containing either the (+)- or the (−)-enantiomer (homochiral[26] comparison set A, Figure 3) leads to generalized cosine β values[27] (GCB = normalized scalar product between two alignment tensors; see section 3 in the Supporting Information) close to one, as expected. The same is true for the homochiral combinations in **p1b** and **p1c** (set B). These experiments not only confirm the reproducibility of the alignment using different phase preparations but also using different polymer preparations. Next, we compared the alignment tensors for the heterochiral[26] combinations in **p1a** (Figure 3, set C). Within this set all possible combinations of two phases containing (−)-IPC with three phases containing (+)-IPC are investigated. The average of the resulting six GCBs was found to be 0.415 which demonstrates a much higher enantiodifferentiating capability of **p1a** as compared to PBLG (Figure 3, set G) with a GCB of 0.991. To our delight with the slightly modified polymers **p1b** and **p1c** this favorable property is even more pronounced (Figure 3, set D). To ensure the reproducibility of this finding we compared the alignment tensors of three samples each containing either (−)-IPC or (+)-IPC in **p1b** and one sample of (+)-IPC in **p1c**.

The averaged GCB of the resulting 12 heterochiral combinations was found to be as low as 0.0362 ± 0.0277

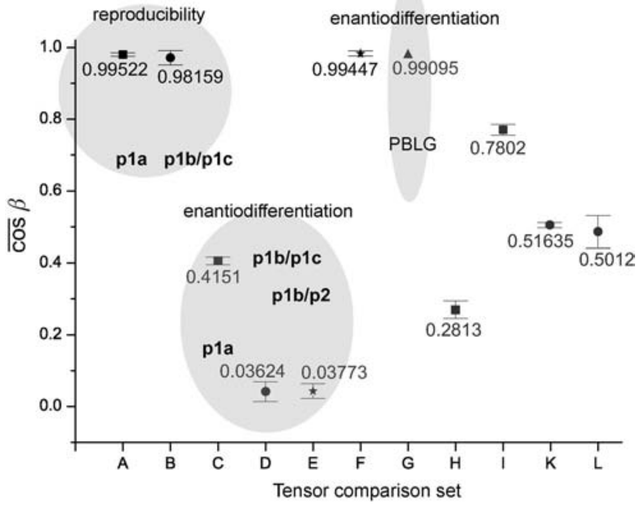


Figure 3. Averaged generalized cosine β values for the different tensor comparison sets. A) Four homochiral combinations in **p1a**. B) Nine homochiral combinations in **p1b/p1c**. C) Six heterochiral combinations in **p1a**. D) Twelve heterochiral combinations in **p1b/p1c**. E) Three homochiral combinations in "enantiomorphous" polymer preparations. F) Four heterochiral combinations in "enantiomorphous" polymer preparations. G) One heterochiral combination in PBLG. H–L) Various homochiral combinations with PBLG to show the different orientation induced by PBLG as compared to the polyacetylenes **p1a–c**. For more details see the Supporting Information.

which means that the alignment tensors of the enantiomers of IPC are almost orthogonal in these media. In the tensor comparison sets C and D the diastereomorphous relation between the analyte and the medium originates from the interaction of both enantiomers of the former with a polymer of a given absolute configuration. Alternatively, this diastereomorphous situation can be generated by the interaction of one enantiomer of IPC with both enantiomers of the polymer (set E). As expected, the GCBs calculated from pairs of tensors derived from RDCs of (−)-IPC in **p1b** and (−)-IPC in **p2a** (opposite helical sense as compared to **p1b**) are close to zero and to the values calculated for set D.

On the other hand, if we use left-handed helical **p2a** containing (−)-IPC and compare the resulting tensors with those calculated from (+)-IPC in right-handed helical **p1b** we found them to be nearly identical (GCBs close to one, set F) as they should be (enantiomorphous combinations). Finally, we compared the alignment properties of PBLG and **p1a**/**p1b**. Interestingly, the PBLG/(−)-IPC and **p1a**/(−)-IPC comparisons (set H) deliver quite different GCBs as compared to the corresponding ones with (+)-IPC as the analyte (set I). This means that for (−)-IPC the orientations in both media are much more different than for (+)-IPC. On the contrary when using **p1b** in the comparisons with PBLG (set K for (−)-IPC, set L for (+)-IPC) the differences in the alignment are independent from the absolute configuration of the analyte (both averaged GCBs have similar values around 0.5). Obviously, this remarkable observation must be somehow related to the different enantiodifferentiating capabilities of **p1a** and **p1b**. This interesting relation may be the clue to optimization strategies aiming either at maximum different alignment properties of two media or at the maximum enantiodifferentiating capability of a given medium.

In conclusion, we have shown that L- and D-valine-derived polyacetylenes **p1** and **p2** are excellent alignment media for the measurement of residual dipolar couplings in $CDCl_3$. They combine narrow line widths from the analyte and optimum alignment strength for the measurement of $^1D_{CH}$ couplings with pronounced enantiodifferentiating capabilities.

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