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Polyguanidines as Chiral Orienting Media for Organic Compounds

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The determination of the three-dimensional structure of organic compounds by NMR spectroscopy usually involves the measurement of ^3J coupling constants,[1] NOE values[2] and to a lesser extent cross-correlated relaxation[3] to obtain information about dihedral angles, distances and projection angles, respectively. If the determination of the relative or even the absolute configuration of stereogenic elements is the goal of the structural investigation the elucidation of conformation and configuration superimpose each other entailing the necessity to determine both structural aspects simultaneously.[4] Especially in cases of conformational flexibility, these conventional NMR restraints often do not lead to unambiguous configurational assignments.

It has recently been shown that residual dipolar couplings (RDCs) can yield information complementary to ^3J couplings and NOE parameters[5,6] and allow the determination of relative configurations even in the presence of (a limited degree of) motion.[7]

RDCs belong to the class of anisotropic NMR parameters and therefore the compound in question needs to be oriented with respect to the magnetic field in order to be able to observe them. Recently, considerable progress has been made in the area of orienting media for compounds, which are not soluble in water.[8] In terms of future applications of RDCs to determine absolute configurations, it is essential that the compound in question is not only aligned with respect to the magnetic field, it is furthermore necessary to induce enantiodifferentiating alignment. This in turn demands the orienting medium to be chiral, non-racemic such that the interactions with the analyte become diastereomorphous and enantiomers give rise to separate sets of signals. There is already one very promising first report by Lesot et al., who were able to determine the absolute configuration of a chiral epoxide based on the comparison of quadrupolar splittings observed for this compound with those for compounds of known absolute configuration.[9]

In addition to enantiodiscrimination and compatibility with organic solvents, the alignment medium should induce weak orientation, such that dipolar couplings in the Hz range are observed ("weak alignment"). This is best fulfilled either by polymer gels[8a–h,10] or by lyotropic liquid crystalline (LC) systems.[11]

Several aqueous chiral lyotropic LC systems have already been used as enantiodiscriminating orienting media.[12] The only known class of chiral orienting media for organic solvents based on lyotropic liquid crystalline (LC) phases are the LC phases of the homopolypeptides poly-γ-benzyl-L/D-glutamate (PBLG/PBDG), poly-γ-ethyl-L-glutamate (PELG/PEDG), and poly-ε-carboxybenzoyl-L/D-lysine (PCBLL/PCBDL).[13,14] These polymeric lyotropic LC systems have the additional advantage that, due to their high molecular weight (M_W), their magnetization relaxes fast and therefore virtually no signal of the orienting medium itself is detected.

The degree of orientation in these media sometimes happens to be too large, complicating the extraction of RDCs. Some of us have shown recently that a significant improvement of spectral quality and reliability of couplings can be achieved, if high molecular weight (M_W) polyglutamates were used.[8i] With increasing M_W the critical concentration for the phase transition of the LC phase drops, which permits measurements at lower polymer concentrations. This in turn has beneficial effects on the line widths and reduces the intensity of residual polymer signals. This dependence, however, occurs only as long as the length of the polymer does not exceed its persistence length.[15]

It has been shown by the group of Courtieu[14c,d] that the enantiodiscrimination in these chiral phases is due to a different orientation of the two enantiomers in the liquid crystalline phase. Recently, we investigated how different the orientations for both enantiomers of isopinocampheol (IPC)

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in polyglutamates are. Interestingly, these orientations are rather similar as can be seen from the eigenvector plots in Figure 1 b.[8j]

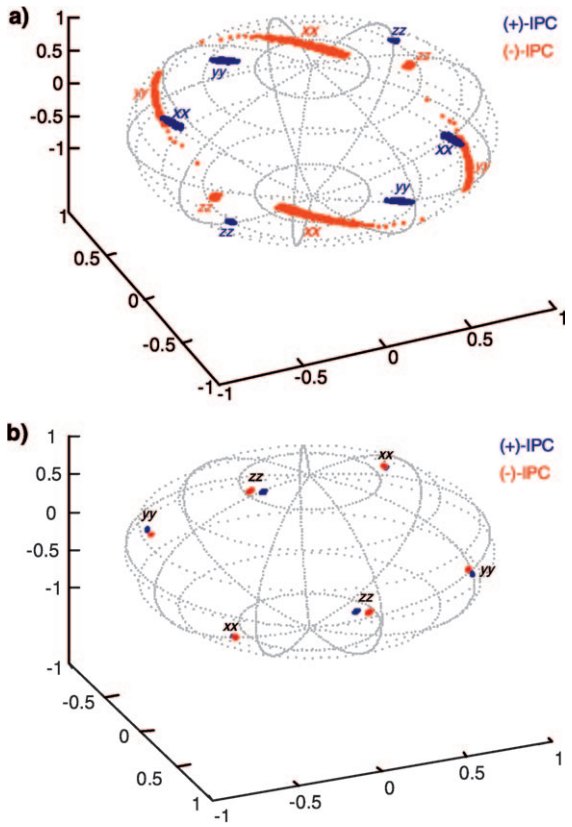
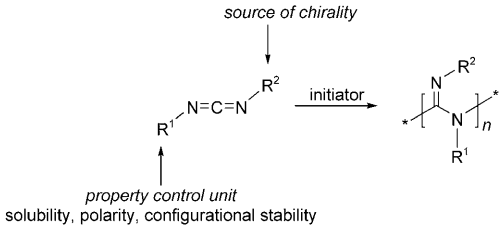


Figure 1. Graphical illustration of the eigenvectors of the Saupe matrix for (+)- and (−)-IPC in a) (*R*)-PPEMG, b) and PBLG.

We wondered whether helically chiral polymers other than homopolypeptides would also allow for the orientation of organic compounds and the discrimination of enantiomers. Thus, we were searching for chiral, non-racemic polymers displaying high persistence lengths capable of forming lyotropic LC phases. These kinds of polymers are expected to be characterized by low critical concentrations, a low induced degree of order for the compound in question ($D_a \approx 1\times10^{-4}$) and enantiodifferentiating properties.

Since many years helically chiral synthetic polymers attract the interest of polymer chemists.[16] Potential applications include enantiomer separations, chirality sensing and asymmetric catalysis. Our interest in these materials began with the idea to develop uniformly configured multiple-site catalysts based on soluble polymers.[17] On the other hand, as rigid-backbone polymers they should form lyotropic liquid crystalline phases[18] which makes them interesting candidates for the development of new chiral alignment media. Indeed, one-handed helical polymers such as polyisocyanates,[19] polyacetylenes,[20] polyisocyanides[21] and polyguanidines[22] do form lyotropic LC phases.

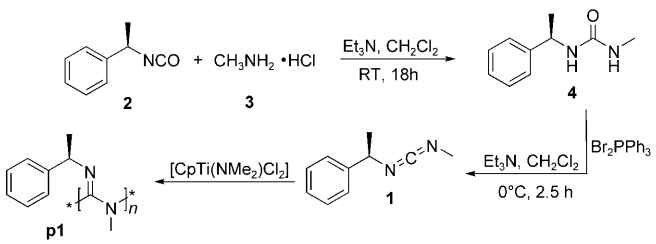
For a number of reasons we decided to work with polyguanidines (Scheme 1). First of all the synthesis of a broad range of symmetrical or unsymmetrical carbodiimide monomers via easy to access ureas or thioureas is straightforward. Helically chiral, configurationally stable polymers are obtained by living polymerization of carbodiimides with chiral substituents.[23] Alternatively, single-handed polymers can be synthesized by screw sense selective polymerization of achiral carbodiimides with chiral titanium complexes.[24] In contrast to polyisocyanates and polyisocyanides, properties such as solubility, polarity and even the configurational stability can be adjusted independently (via R^1) from structural features controlling the helical sense (via R^2). Polyguanidines are intrinsically stiffer than polyisocyanates and form anisotropic phases at rather low concentrations[22b] in a variety of non-polar solvents.



Scheme 1. Synthesis and structure of polyguanidines.

Finally, polyguanidines with low helix inversion barriers and chiral side chains can be thermally equilibrated to the thermodynamically more stable helix conformation.[22c,25] Note that the helix inversion barriers and therefore the distinction between stiff or dynamic helices in polyguanidines depend on the side chains.

The polyguanidine investigated here, poly-(*N*-methyl-*N*′-((*R*)-1-phenylethyl)guanidine ((*R*)-PPEMG, **p1**), is known to exhibit cholesteric liquid crystalline phases in chloroform at 12.5 % *w*/*w*.[22b] The carbodiimide monomer **1** was obtained by bromotriphenylphosphonium bromide mediated dehydration[26] of the corresponding urea **4**, which was obtained from the enantiopure isocyanate (**2**) by reaction with methylammonium chloride (**3**).[27] The enantiopure carbodiimide **1** was subjected to a living polymerisation using the titanium complex [CpTi(NMe_2)Cl_2] (**5**)[23a,b,28] as initiator (Scheme 2).



Scheme 2. Synthesis of *N*-methyl-*N*′-((*R*)-1-phenylethyl)carbodiimide (**1**) and the corresponding polymer **p1**.

We conducted polymerisations at different monomer to initiator ratios and determined the M_W values of the resulting polymers via GPC (Table 1, for experimental details see Supporting Information). As expected, with increasing monomer to initiator ratios the molecular weights of the polymers increased (Table 1) and the liquid crystalline phase can be observed at lower concentrations. The completeness of the phase transition was judged from the disappearance of the isotropic ^{2}H NMR signal (singlet) of the solvent ($CDCl_3$) and its replacement by a doublet split by the minimum quadrupolar coupling ($\Delta\nu_{Q,min}$) characterizing the anisotropic phase. This molecular weight dependence of the minimum lower concentration to reach the anisotropic state is in accordance with calculations by DuPré[15] and also corroborates our experimental findings with PBLG.[8i]

Table 1. Polymerisations of carbodiimide **1** with titanium complex **5**.

Polymer	[M]/[I][a]	Yield [%]	M_n[c] [g mol^{-1}]	M_w[d] [g mol^{-1}]	PDI[e]	(w/w)[f] [%]
p1-1	80:1	65	10002	17886	1.79	26.1[g]
p1-2	100:1	98[b]	15964	20978	1.31	n.d.[h]
p1-3	250:1	82	43931	104460	2.38	18.7[i]

[a] Monomer to initiator ratio. [b] Polymer contaminated by unknown impurities. [c] Number average molecular weight, calibrated against polystyrene standards. [d] Weight average molecular weight, calibrated against polystyrene standards. [e] PDI (polydispersity index) = M_w/M_n. [f] Critical concentration for the liquid crystalline phase in $CDCl_3$ in weight percent as determined by ^{2}H NMR spectroscopy. [g] $\Delta\nu_{Q,min}(CDCl_3)$ = 540 Hz (303 K). [h] Not determined. [i] $\Delta\nu_{Q,min}$ ($CDCl_3$) = 1077 Hz (303 K).

Contrasting our experiences with PBLG it is worth mentioning here that with the low molecular weight polymer **p1-1** a lower $\Delta\nu_{Q,min}$ (compared with **p1-3**) was measured at a higher polymer concentration.

As reported by Novak et al.,[23a] polyguanidines tend to absorb on the chromatography columns used in gel permeation chromatography (GPC), which leads to pronounced peak broadening and to non-reliable PDIs. We managed to reduce the absorption of the polymer significantly when using diethanolamine (DEA) as an additive (see Supporting Information), but the PDIs reported above are still affected by that phenomenon and therefore molecular weight distributions are expected to be smaller than those reported in Table 1.

The resulting (R)-PPEMGs exhibit negative Cotton effects at λ = 262 nm in their CD spectra (see Supporting Information) with molar ellipticities comparable to those reported in the literature (e.g., θ_{262} = −3872.35 mdeg m^2 mol^{-1} for **p1-3** in Table 1), which are assigned to P helices.[27]

We chose the polymer sample with highest molecular weight (**p1-3**) for the investigations towards the adequacy of polyguanidines as orienting media.

It exhibits a liquid crystalline phase at a critical concentration of 18.7% w/w in $CDCl_3$ (monitored by observation of the concentration dependence of the ^{2}H spectra) with a quadrupolar splitting of the solvent signal of 1077 Hz.[30] To study the alignment properties of (R)-PPEMG and to be able to compare it to PBLG, we chose isopinocampheol (IPC) as the analyte. To maintain stable liquid crystalline phases all measurements were conducted at concentrations slightly above the critical concentration (see Table S4 for more information concerning the exact composition of the samples). The two enantiomers of IPC were oriented in (R)-PPEMG and RDCs were extracted from ω_1-coupled HSQCs[31] (Figure 2). Due to the rather strong orientation induced (axial component of the alignment tensor D_a = 2.7 × 10^{-3} for the phase containing (−)-IPC after normalisation to the quadrupolar splitting of (+)-IPC (see below) and D_a = 2.3 × 10^{-3} for (+)-IPC), lines are rather broad. The total couplings, scalar couplings and re-

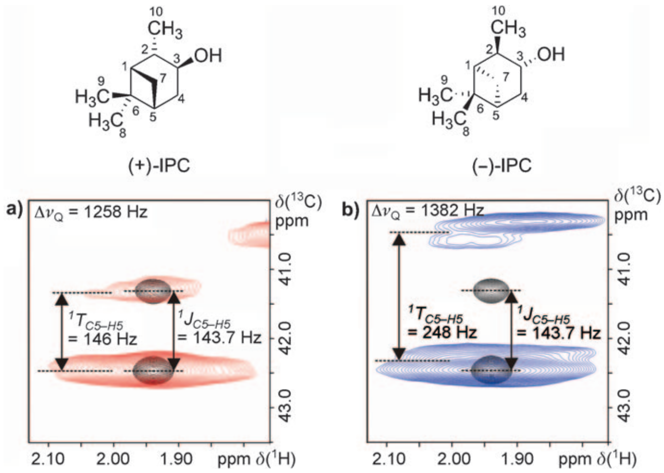


Figure 2. Sections (corresponding to the C5-H5 cross peak) of ω_1-coupled HSQCs of a) (+)-IPC and b) (−)-IPC in the liquid crystalline phase of (R)-PPEMG in $CDCl_3$. The isotropic spectrum is shown in black for comparison. Note that the additional splitting in ω_1 observable in b) is due to long-range C–H coupling.[29]

Table 2. Scalar (J), total (T) and dipolar (D) one bond couplings ($^1T_{C-H} = {}^1J_{C-H} + 2\cdot{}^1D_{C-H}$) of (+)- and (−)-IPC in (R)-PPEMG. Each splitting was evaluated three times. The error given is the difference between the largest and smallest value extracted (maximum difference) in the three measurements (divided by 2 for D).

Spin pairs[b]	$^1J_{CH}$ [Hz]	(+)-IPC $^1T_{CH}$ [Hz]	$^1D_{CH}$ [Hz]	(−)-IPC[a] $^1T_{CH}$ [Hz]	$^1D_{CH}$ [Hz]
C1–H1	139.5 ± 0.5	216 ± 6	38 ± 3	157 ± 4	9 ± 2
C2–H2	125.8 ± 0.5	152 ± 2	13 ± 1	150 ± 8	12 ± 4
C3–H3	139.6 ± 0.5	271 ± 2	66 ± 1	268 ± 2	64 ± 1
C4–H4s	126.0 ± 0.5	250 ± 4	62 ± 2	206 ± 10	40 ± 5
C4–H4a	126.0 ± 0.5	110 ± 2	−8 ± 1	100 ± 4	−13 ± 2
C5–H5	143.7 ± 0.5	146 ± 2	1 ± 1	248 ± 10	52 ± 5
C8–H8	123.0 ± 0.5	169 ± 2	23 ± 1	172 ± 2	25 ± 1
C9–H9	124.6 ± 0.5	85 ± 4	−20 ± 2	94 ± 2	−15 ± 1
C10–H10	124.4 ± 0.5	108 ± 2	−8 ± 1	87 ± 2	−18 ± 1

[a] As the two samples used where not identically concentrated the total and dipolar couplings of (−)-IPC were normalized by the ratio of quadrupolar splittings of the two samples ($^1D_{(-)\text{-IPC,norm}} = {}^1D_{(-)\text{-IPC,meas}}$* 1258/1382) in order to provide comparability. [b] The total and dipolar couplings for C7–H7$_{a/s}$ are not observable.

sidual dipolar couplings of (+) and (−)-IPC in (*R*)-PPEMG are listed in Table 2.

As can clearly be seen, the observed total and dipolar couplings are significantly different for the two enantiomers of IPC in the helically chiral polymeric lyotropic liquid crystal. Thus enantiodiscrimination is taking place. The RDCs reported in Table 2 were used for the calculation of the order tensors of the two enantiomers applying the RDC module of hotFCHT[32] in order to find out how large the difference in orientation for the two enantiomers of IPC in (*R*)-PPEMG is. The results of these calculations are compiled in Table 3 and the difference in orientations is graphically illustrated in Figure 1a. The eigenvectors of the Saupe matrix for all four possible orientations of each (+) and (−)-IPC are shown as intersections with a sphere of radius unity for both media. The uncertainties of the eigenvectors were determined by a Monte-Carlo based method.[33,34] As can be taken from Figure 1a the S_{zz} component is determined most precisely, reflected by its narrow distribution on the surface of the sphere.

Table 3. Orientational properties of (−)-IPC and (+)-IPC in (*R*)-PPEMG.

$\Delta\nu_Q$ [Hz][b]	D_a [10^{-3}][c]	α [°][d]	β [°][d]	γ [°][d]
		(−)-IPC[a]		
1382	2.70[e]	33.8 ± 0.46	78.3 ± 0.74	175.1 ± 7.8
		(+)-IPC[f]		
1258	2.30	39.8 ± 0.44	84.5 ± 0.37	118.8 ± 1.8

[a] 42 mg (−)-IPC, 123.4 mg (*R*)-PPEMG, 405 mg $CDCl_3$ (21.6% *w*/*w* polymer. [b] Absolute value of the quadrupolar splitting of the solvent. [c] Axial component of the orienting tensor. [d] Euler angles relating the principal axis system and the initial molecular axis frame. [e] After normalisation with the ratio of quadrupolar splittings (see footnote of Table 2). [f] 42 mg (+)-IPC, 145.8 mg (*R*)-PPEMG, 494 mg $CDCl_3$ (21.4% *w*/*w* polymer).

On the other hand, from the rather broad distribution of the corresponding eigenvectors on the sphere, it is obvious that the S_{xx} and S_{yy} components[35] (especially for (−)-IPC) are less well defined for (*R*)-PPEMG. Nevertheless, the difference in orientations for (+) and (−)-IPC is obviously significant. Interestingly, this difference and therefore also the enantiodiscriminating power of the orienting medium (*R*)-PPEMG for IPC seems to be larger than the one of PBLG (see Figure 1b), in which differences in orientations were rather small.[8j] Whether this is also the case with other solutes, is currently under investigation.

In summary, we have presented a member of a new class of chiral, enantiodiscriminating orienting media for organic compounds based on helically chiral polyguanidines. Although RDCs obtained are rather large, which is an aspect we want to improve in the future, the orientations of the two enantiomers of IPC are clearly different and can be determined reliably. For IPC the difference in orientation observed in (*R*)-PPEMG appears to be larger than the one observed in PBLG. This will be essential for the development of a method to determine absolute configurations of chiral, non-racemic compounds. Future work will be directed toward the development of polymers with enhanced stiffness to reduce the critical concentration needed to reach the anisotropic state by enhancing the steric bulk of the side chains. Moreover, we try to separate the alignment properties from enantiodifferentiation by embedding of the helically chiral polymers into polymer gels. This may entail the opportunity to induce alignment by strain,[8a–h] thus avoiding the necessity to prepare a LC phase, and enantiodifferentiation by the embedded helical structures.

Experimental Section

See Supporting Information.

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Keywords: alignment media · liquid crystals · NMR spectroscopy · polyguanidines

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