CHEMISTRY
A EUROPEAN JOURNAL

Supporting Information

^{2}H NMR Studies of Two-homopolypeptide Lyotropic Enantiodiscriminating Mesophases: An Experimental Quantification of Solute-Fiber Affinities

Philippe Lesot*,[a], Olivier Lafon[a], Christie Aroulanda[b] and Ronald Y. Dong[c]

[a] Dr. Philippe Lesot, Dr. Olivier Lafon

Laboratoire de Chimie Structurale Organique, RMN en Milieu Orienté, Université de Paris-Sud (XI), ICMMO, UMR CNRS 8182, Bât. 410, F-91405 Orsay cedex, France.

Fax: (+33) 169-15-81-05 / Tel: (+33) 169-15-47-59 / E-mail : philesot@icmo.u-psud.fr

[b] Dr. Christie Aroulanda

Equipe de Méthodologie RMN, Nancy-Université, SRSMC, UMR CNRS-UHP 7565, BP 239, F-54506 Vandoeuvre-lès-Nancy cedex.

[c] Prof. Ronald Y. Dong

Department of Physics and Astronomy, University of British Columbia, Vancouver, BC, Canada V6T 1Z1.

Analysis of NMR results in achiral oriented mixtures. So far, mixtures of polypeptides in solution were only employed to provide achiral liquid-crystalline phases where any enantiodiscrimination disappears.[1,2] These compensated mixtures are prepared by mixing equal amounts by weight of polypeptides of same nature but with opposite stereochemical absolute configuration (*e.g* PBLG and its enantiomer PBDG, or PCBLL and PCBDL).[1,2] These achiral mesophases are noted "PBG" and "PCBL", respectively. In these mixtures, both antipodes of a chiral molecule -hereafter denoted for sake of simplicity *l* and *d*, and without any link to absolute stereodescriptor- exchange rapidly, on the NMR time scale, between the *L*- and *D*- helical vicinities of each polypeptide. This results in identical average magnetic interactions for enantiomer solutes, and no difference on their NMR spectra is expected.[2] Conceptually, the disappearance of the enantiodiscrimination can be seen as follows.

Because the physical interactions at molecular level are invariant by symmetry, the homochiral (resp. heterochiral) diastereoisomeric interaction potentials in the PBDG and PBLG phases, denoted «$d^{\text{solute}}\cdots D^{\text{polypeptide}}$» and «$l^{\text{solute}}\cdots L^{\text{polypeptide}}$», (resp. «$l^{\text{solute}}\cdots D^{\text{polypeptide}}$» and «$d^{\text{solute}}\cdots L^{\text{polypeptide}}$»), are symmetrical to each other as depicted in Figure SI-1a. Thus from the ^{2}H NMR point of view, the strict inversion of interaction potentials in PBLG and PBDG leads to simply interchange the spectrum of each enantiomer (see Fig. SI-1b). In a racemic mixture of enantiomeric polypeptides, the overall interactions undergone by the *d* solute («$d^{\text{solute}}\cdots D^{\text{polypeptide}}$» $^{+}$«$d^{\text{solute}}\cdots L^{\text{polypeptide}}$») and the *l* solute («$l^{\text{solute}}\cdots L^{\text{polypeptide}}$» $^{+}$ «$l^{\text{solute}}\cdots D^{\text{polypeptide}}$») become equal. Hence in the fast exchange regime (experimental cases), no enantiomeric discrimination is possible to be detected on the NMR time scale.

Analytically, the comparison of NMR spectra recorded in the achiral phase with those obtained in the chiral phases allows one to understand readily the latter, because the spectral enantiodiscriminations have disappeared while the spectral diastereodiscriminations are still active. Moreover, for ^{2}H spectra, it is possible to determine the relative sign of quadrupolar splittings (see Fig. SI-1b) associated to enantiomeric or enantiotopic direction pairs. Indeed the $\Delta\nu_Q$'s values measured in the achiral mesophase (denoted $\Delta n_Q(L+D)$) are equal to the average of values obtained in the PBLG or PBDG chiral mesophases (denoted $\Delta\nu_Q^{\text{aver}}$). This equality can be easily demonstrated. For instance, in the PBLG phase, we can write:

$$\Delta\nu_Q^{\text{aver}} = \left(\frac{\Delta\nu_Q^l(L)+\Delta\nu_Q^d(L)}{2}\right) = \frac{3}{2}C_Q \times \left(\frac{S^l(L)+S^d(L)}{2}\right) \qquad \text{(SI-1)}$$

In this equation, $S^l(L)$ and $S^d(L)$ are the order parameters of the C-D bond that derive from interactions between the *l* (resp. *d*) enantiomer(s) and the polypeptide of *L* configuration. The same kind of average can be defined in the PBDG phase, except that the *L* stereodescriptor is replaced by the *D* stereodescriptor. On the other hand, in the achiral PBG phase, the order parameter for a given C-D bond results in the average of order parameters of the *l* (resp. *d*) enantiomer interacting with the *L* and *D* helices if we assume that the residence times of *l* and *d* stereoisomers in the vicinity of PBLG and PBDG are identical. Thus we can write:

$$\mathrm{S}^{l}(L+D)=\frac{\mathrm{S}^{l}(L)+\mathrm{S}^{l}(D)}{2} \quad \text{and} \quad \mathrm{S}^{d}(L+D)=\frac{\mathrm{S}^{d}(L)+\mathrm{S}^{d}(D)}{2} \tag{SI-2}$$

From symmetry considerations, the term $S^l(D)$ (resp. $S^l(L)$) is actually identical to the term $S^d(L)$ (resp. $S^d(D)$), and so, we can write this series of equalities:

$$\begin{aligned}\mathrm{S}^{l}(L+D)&=\frac{\mathrm{S}^{l}(L)+\mathrm{S}^{l}(D)}{2}\\&=\frac{\mathrm{S}^{l}(L)+\mathrm{S}^{d}(L)}{2}=\mathrm{S}^{\mathrm{aver}}(L)\\&=\frac{\mathrm{S}^{d}(D)+\mathrm{S}^{l}(D)}{2}=\mathrm{S}^{\mathrm{aver}}(D)\\&=\frac{\mathrm{S}^{d}(D)+\mathrm{S}^{d}(L)}{2}=\mathrm{S}^{d}(L+D)\end{aligned} \tag{SI-3}$$

From Equations. 1 (main text), SI-1 and SI-3, we can conclude that :

$$\Delta n_{\mathrm{Q}}^{l\ \mathrm{or}\ d}(L+D)=\Delta n_{\mathrm{Q}}^{\mathrm{aver}}=\frac{\Delta n_{\mathrm{Q}}^{l}(L)+\Delta n_{\mathrm{Q}}^{l}(L)}{2}=\frac{\Delta n_{\mathrm{Q}}^{d}(D)+\Delta n_{\mathrm{Q}}^{d}(D)}{2}. \tag{SI-4}$$

Note that the same phenomenon arises for enantiotopic directions in prochiral molecules dissolved in a PBG or PCBL mixture.[1,2]

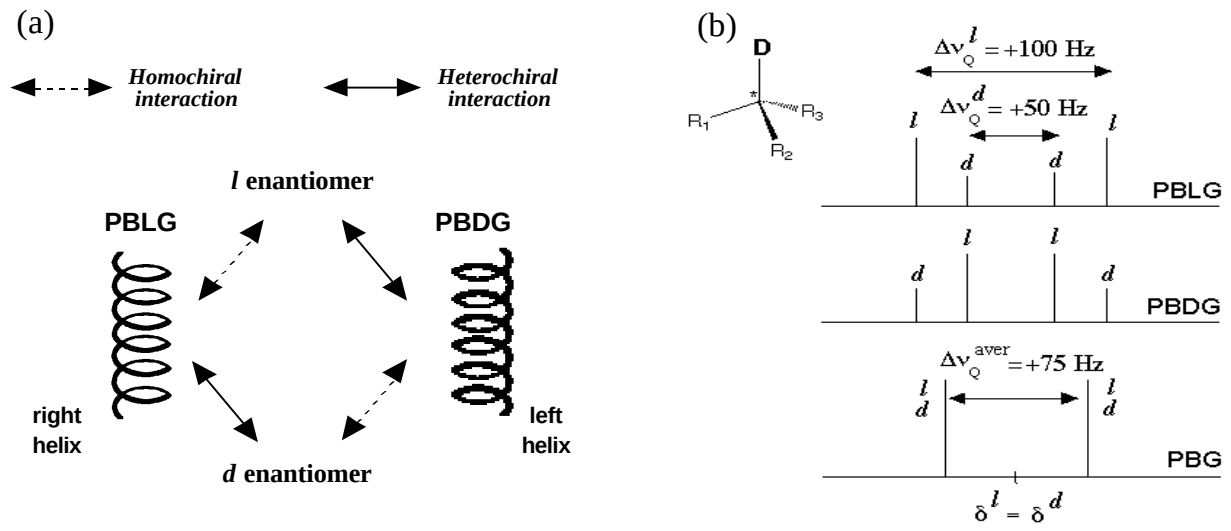

Figure SI-1. a) Definition of homo- and heterochiral interactions involved between *l* and *d* enantiomers and the PBLG or PBDG helices in a PBG mixture. b) Schematic evolution of ^{2}H-{^{1}H} spectra associated to a monodeuterated chiral molecule (enriched in *l* isomer) dissolved in the PBLG phase (top), the PBDG phase (middle) and PBG (bottom) phases. The strict inversion of interaction potentials in PBLG and PBDG leads to interchange the spectrum of each enantiomer. Here we assumed that the sign of the $\Delta\nu_Q$'s were identical. Opposite sign would lead to a value for $\Delta\nu_Q$ equal to ± 25 Hz. Note that the $\Delta\nu_Q$ values and the *d*,*l* assignment are arbitrary. In figure 1b, we assume $\delta^l = \delta^d$.

Establishing Equation 2 and 3 of the main text. The prediction of $\Delta\nu_Q$ or $1/T_{1Z}$ for a solute embedded in a liquid crystal requires the calculation of an ensemble average. For a system containing N molecules (solute, co-solvent and polypeptide molecules), denoted as 1 to N, the average value, <A>, of any single molecule property, A, can be defined as (for a molecule denoted 1):[3]

$$\langle A \rangle = \int_{sample} A\, f(X_1) dX_1 . \qquad \text{(SI-5)}$$

Here X_1 denotes the set of variables characterizing the molecule 1, $f(X_1)dX_1$ is the probability to find the coordinates of the molecule 1 located between X_1 and $X_1 + dX_1$. For the quadrupolar splitting, we must evaluate the ensemble average of $A = [3\cos^2(q_{CD}) - 1]/2$ (see Eq. 1) whereas for the autocorrelation function, this ensemble average is applied to the quantity $D^{2*}_{0,n}(t)D^{2}_{0,n}(0) - \left|\langle D^{2}_{0,n}\rangle\right|^2$.

In the framework of hypotheses 1 and 2, the mesophase can be described using a periodic hexagonal minimal «box», whose dimensions are equal to the length $d_{fiber\text{-}fiber}$, and containing a single fragment of *a* or *b* polypeptide placed at its center. For a «neat» mesophase (i.e. containing only a single kind of

polypeptide *a* or *b*), the periodic repetition of one box allows us to describe the whole sample and Eq. SI-5 can be simplified into:

$$\langle A \rangle_{a \text{ or } b} = \int_{box} A f_{a \text{ or } b}(X_1) dX_1 \qquad \text{(SI-6)}$$

Conversely, for a binary mixture of polypeptides, two boxes must be considered, one for the *a* polypeptide (*a* box) and one for the *b* polypeptide (*b* box), and hence the integral over the whole sample in Eq. SI-5 now splits into two integrals:

$$\langle A \rangle_{mix} = P_a^{solute} \int_{box} A f_{a,box}(X_1) dX_1 + P_b^{solute} \int_{box} A f_{b,box}(X_1) dX_1 \qquad \text{(SI-7)}$$

where P_a^{solute} (resp. P_b^{solute}) is the probability for a solute to be closer to the *a* (resp. *b*) *a*-helix than the *b* (resp. *a*) *a*-helix. These probabilities depend on the relative proportion of solute (and co-solvent) within the two boxes, namely the molecular distribution of solute around each fiber.

Under the hypothesis 3, the molecular compositions of boxes *a* and *b* are identical to those of the minimal boxes used to simulate the «neat» mesophases (*a* or *b*). Therefore, the first (resp. second) integral in Eq. SI-7 is equal to $<A>_a$ (resp. $<A>_b$). Furthermore, the solute probability P_a^{solute} (resp. P_b^{solute}) are equal to the molar fraction of *a* (resp. *b*) peptide units, x_a^{pu} and x_b^{pu}. Consequently, Eq. SI-7 can be recast into :

$$\langle A \rangle_{mix} = x_a^{pu} \langle A \rangle_a + x_b^{pu} \langle A \rangle_b = x_a^{pu} (\langle A \rangle_a - \langle A \rangle_b) + \langle A \rangle_b \qquad \text{(SI-8)}$$

which is denoted Eq. 2 in the main text.

Under the condition of hypothesis 4, the probabilities P_a^{solute} and P_b^{solute} ($P_a^{solute} + P_b^{solute} = 1$) differ from x_a^{pu} and x_b^{pu}, and so Eq. 2 in the main text is not valid anymore. P_a^{solute} and P_b^{solute} could be expressed as function of the amount of solute in each box, $n_{a \text{ or } b,box}^{solute}$, (in mol) and the number of boxes, $n_{a \text{ or } b}^{box}$, for each polypeptide in the whole sample. However, as $N_{a \text{ or } b}^{box}$ is proportional to the number of peptide units for each polypeptide and as the number of peptide unit is identical in each box, P_a^{solute} and P_b^{solute} are expressed as:

$$P_{a\ or\ b}^{solute} = \frac{n_{a\ or\ b,box}^{solute} N_{a\ or\ b}^{box}}{\left(n_{a,box}^{solute} N_{a}^{box} + n_{b,box}^{solute} N_{b}^{box}\right)} = \frac{n_{a\ or\ b,box}^{solute} n_{a\ or\ b}^{pu}}{\left(n_{a,box}^{solute} n_{a}^{pu} + n_{b,box}^{solute} n_{b}^{pu}\right)} \quad \text{(SI-9)}$$

where $n_{a\ or\ b,box}^{solute}$ is the amount of solute within each box and $n_{a\ or\ b}^{pu}$ is the amount of *a* or *b* peptide units (in mol).

In the ideal conditions of an infinite dilution which allows solute-solute interactions to be disregarded (hypothesis 5), Eq. SI-7 can be simply recast to now read:

$$\langle A \rangle_{mix} = \frac{c_{a,box}^{solute} x_{a}^{pu}}{\left(c_{a,box}^{solute} x_{a}^{pu} + c_{b,box}^{solute} x_{b}^{pu}\right)} \langle A \rangle_{a} + \frac{c_{b,box}^{solute} x_{b}^{pu}}{\left(c_{a,box}^{solute} x_{a}^{pu} + c_{b,box}^{solute} x_{b}^{pu}\right)} \langle A \rangle_{b} \quad \text{(SI-10)}$$

where $n_{a\ or\ b,box}^{solute}$ in Eq. SI-9 is replaced by the concentration of solute within each box, $c_{a\ or\ b,box}^{solute}$, as the boxes *a* and *b* have identical volumes.

By introducing the molar fractions of solute, $k_a = c_{a,box}^{solute} / \left(c_{a,box}^{solute} + c_{b,box}^{solute}\right)$ and $k_b = 1 - k_a = c_{b,box}^{solute} / \left(c_{a,box}^{solute} + c_{b,box}^{solute}\right)$ in the boxes *a* and *b*, respectively, instead of the concentrations, the previous equation becomes:

$$\langle A \rangle_{mix} = \frac{k_a x_{a}^{pu}}{\left(k_a x_{a}^{pu} + k_b x_{b}^{pu}\right)} \langle A \rangle_{a} + \frac{k_b x_{b}^{pu}}{\left(k_a x_{a}^{pu} + k_b x_{b}^{pu}\right)} \langle A \rangle_{b} . \quad \text{(SI-11)}$$

This equation is denoted Eq. 3 in the main text.

Analysis of toluene and phenol. The deuterium spectral data for the samples of toluene and phenol are listed in Table SI-1.

Table SI-1. Spectral data for toluene and phenol dissolved in the PBLG, PCBLL and the MIX mesophases at 300 K

Compd	Deuteron site	δ / ppm[a] *(iso)*	δ / ppm[b] *(aniso)*	$\Delta\nu_Q$ / Hz PBLG (exp.)	$\Delta\nu_Q$ / Hz PCBLL (exp.)	$\Delta\nu_Q$ / Hz MIX (exp.)	$\Delta\nu_Q$ / Hz MIX (expected)[c]	$\lvert\Delta\Delta\nu_Q\rvert$[d] / Hz	Deviation / %
Toluene	Methyl	2.34	2.53	–105 ± 3	–55 ± 5	–83 ± 4	–82	1	1
	Ortho	7.04	7.42	–42 ± 2	+97 ± 7	+24 ± 3	+21	3	12
	Meta	7.15	7.50	–51 ± 2	+98 ± 7	+18 ± 2	+17	1	6
	Para	7.06	7.41	+365 ± 6	+218 ± 10	+301 ± 8	+298	3	<1
Phenol	Ortho	6.73	7.00	+1198 ± 10	–1332 ± 7	–414 ± 7	+47	461	11
	Meta	7.11	7.31	+1215 ± 10	–1271 ± 7	–355 ± 6	+84	439	24
	Para	6.80	7.03	+653 ± 8	–4111 ± 13	–2269 ± 11	–1515	754	33

[a] Data from ACD prediction software. [b] $\delta(CHCl_3)$ is calibrated at 7.30 ppm in anisotropic phase. [c] Value expected from Eq. 2.

[d] $|\Delta\Delta\nu_Q| = |\Delta\nu_Q^{MIX}\ \text{(experimental)} - \Delta\nu_Q^{MIX}\ \text{(expected)}|$.

Analysis of (±)-phenethyl alcohol-d_1. The theoretical and experimental evolution of ^2H quadrupolar splittings of pha *vs.* x^{pu}_{PBLG} is reported in Figure SI-2.

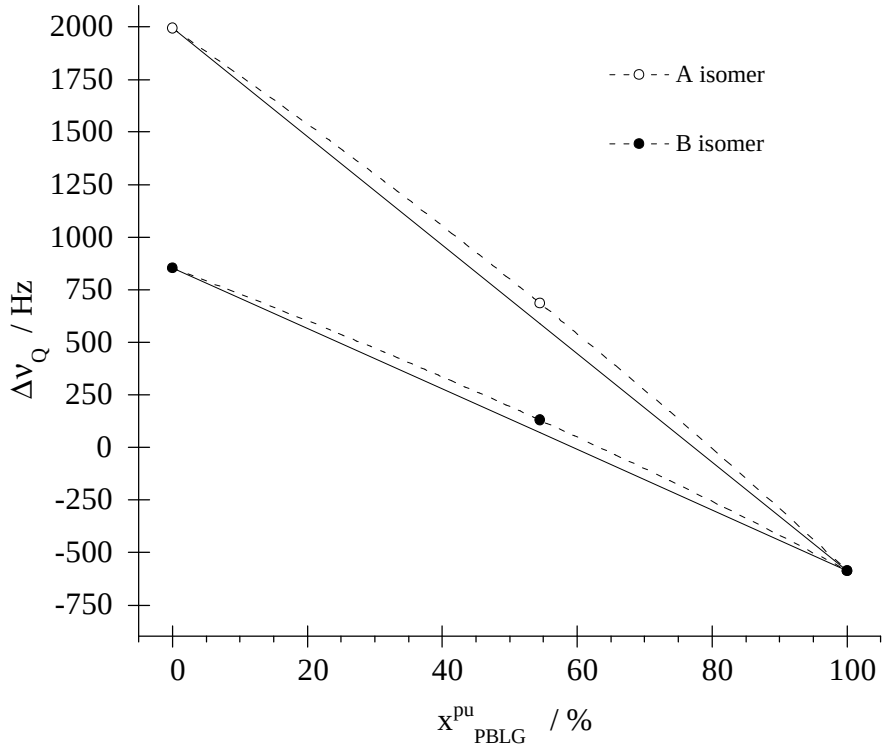

Figure SI-2. Theoretical and experimental evolution of ^2H quadrupolar splittings for pha *vs.* x^{pu}_{PBLG}. The continuous and dashed lines correspond to the fit of experimental data using Eq. 2 when $\langle A \rangle = \Delta\nu_Q$ and Eq. 5, respectively.

Analysis of mixtures of polypeptides with a strong difference in their degree of polymerization. To assess the valid domain of the hypothesis 2, we have studied mixtures made by adding two polypeptides with a large difference in their DP (DPs ratio around a factor 10). Here the central question is to establish if such mixtures still provide homogeneous and monophasic oriented media. In practice, we have prepared a sample made of 50% of PBLG of low DP (DP = 114) and 50% of PCBLL of high DP (DP = 1100) (Tables SI-2 and SI-3, sample 18). The analysis of ^{2}H-{^{1}H} spectrum of bza (enriched in ^{13}C) at 300 K shows a biphasic system where an anisotropic part co-exists with an isotropic part (Fig. SI-3a). The integration of peaks belonging to each region leads to a ratio of 55/45 in favour of the anisotropic part. Data related to this sample are reported in Table SI-2. Note here that using the same component concentrations as in sample 2 but with DP = 114 (Tables SI-2 and SI-3, sample 19), we obtain a biphasic solvent with 98% of isotropic phase.

To estimate the exchange rate of the solute between the isotropic and anisotropic regions (sample 18), the ^{2}H 2D exchange spectroscopy (EXSY 2D experiments) was explored by using three mixing times: 5, 50, 200 ms.[4] Whatever the mixing time set in the EXSY sequence, no exchange cross-peaks between isotropic and anisotropic signals have been detected. This suggests that the exchange of the solute between the isotropic and anisotropic regions is likely slower than the millisecond time scale. A possible cause could be a strong isotropic-nematic interfacial tension, γ_{NI}, existing in these polypeptide biphasic samples.[5, 6]

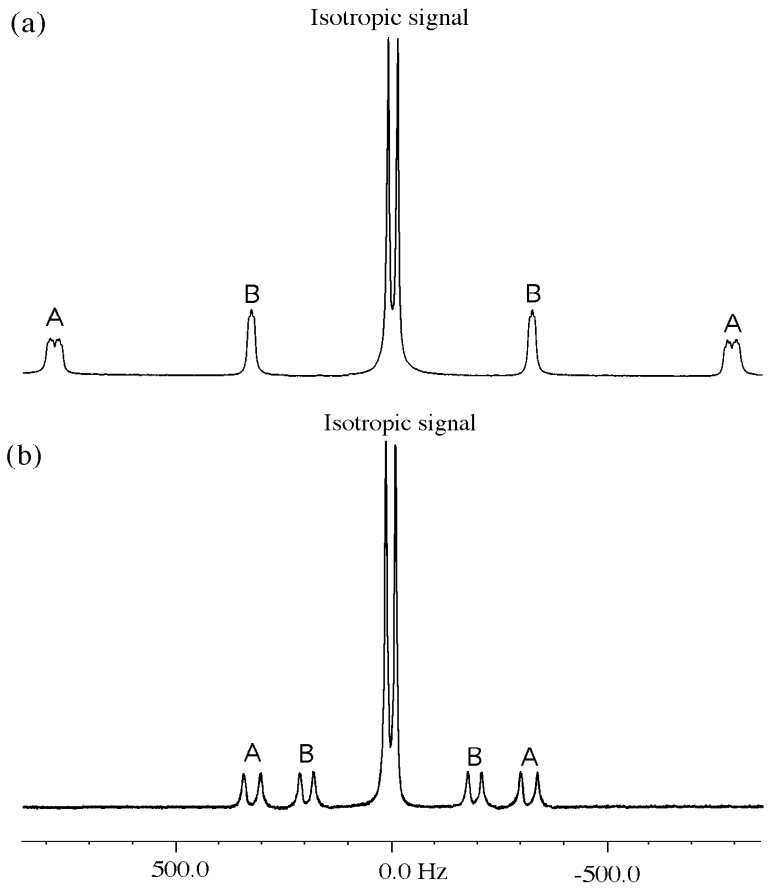

Figure SI-3. 61.4 MHz ^{2}H-{^{1}H} spectrum of bza (enriched in ^{2}H and ^{13}C in methylene group) at 300 K dissolved in a mixture made by equal amounts by weight of PBLG (DP = 114) and PCBLL (DP = 1100) in chloroform a) and of PBLG (DP = 114) and PBLG (DP = 1352) in chloroform b). In both spectra, the central doublet ($^{1}J_{CD}$ = 22 Hz) corresponds to the isotropic ^{2}H signal.

Table SI-2. Spectral data recorded at 300 K for samples 18 to 21

Sample	% in PBLG / PCBLL	% in isotropic region	$\lvert T_{CHCl_3}\rvert$ / Hz	$\lvert D_{CHCl_3}\rvert$ / Hz	$\Delta\nu_Q^A$ / Hz	$\Delta\nu_Q^B$ / Hz	$\lvert\Delta\Delta\nu_Q\rvert$ / Hz	$\lvert T_{DD}\rvert$ /Hz	$\lvert T_{CD}^A\rvert$ / Hz	$\lvert T_{CD}^B\rvert$ / Hz	T_{1Z}^{aver} / ms
18[a]	50 / 50[b]	45%	364	77	–1517	–623	894	9	17	5	176 / (236)[d]
19[a]	100 / 0[b]	> 98%	369 / (210) [c]	79	+418	+187	231	< LW	27	32	No data / (272)
20	0 / 50[b]	> 95%	264 / (210)	27	-668	–286	382	< LW	-	-	No data
21[a]	100 / 0[c]	33%	372 / (210)	81	+638	+388	250	< LW	39	32	290 / (278)

[a] Benzylic alcohol enriched in ^{13}C in the methylene group. [b] Sample made with PBLG with DP = 114 and/or PCBLL with DP = 1100. [c] Sample made with 50 mg of PBLG (DP = 114) and 50 mg of PBLG (DP = 1352). [d] All data associated to isotropic signals are given in parenthesis

The values of $\Delta\nu_Q$ and T_{1Z} measured in the anisotropic region for sample 18 at 300 K (Table SI-2, entry 1) differ significantly from values obtained with sample 5 (Table 1, entry 5b) and sample 7 (see Table 1, entry 7b). Interestingly, these values are not equal any more to the average of values measured in the «neat» PCBLL (see Table 1, entry 7b) and in isotropic phase (see Table 1, entry 1b). If this was the case, we should find that: $\Delta\nu_Q^A$ = –894 Hz, $\Delta\nu_Q^B$ = –364 Hz and T_{1Z} = 351 ms. Actually, the values measured in the sample 18 suggest that a part of PBLG fibers co-exists with PCBLL fibers in the anisotropic regions of the sample. In this case, the values of $\Delta\nu_Q$ and T_{1Z} observed in the anisotropic regions would depend on the amount of PBLG polypeptide unit, x_{PBLG}^{pu}, present in the anisotropic phase (see above) as in the case of a monophasic mixture of polypeptides with high DP. Using the theoretical variations of $\Delta\nu_Q$ and $1/T_{1Z}$ described in the framework of hypothesis 4, it is possible to determine the fraction, x_{PBLG}^{pu}, in the anisotropic regions by recasting Eq. 4 (main text) as:

$$\left(x_{PBLG}^{pu}\right)^{aniso\ phase} = \frac{\langle A\rangle_{PCBLL} - \langle A\rangle_{mix}}{K\left(\langle A\rangle_{mix} - \langle A\rangle_{PBLG}\right) + \langle A\rangle_{PCBLL} - \langle A\rangle_{mix}} \qquad \text{(SI-12)}$$

where <A> is either $\Delta\nu_Q$ or $1/T_{1Z}$.

At 300 K using quadrupolar splitting data extracted from monophasic samples 1 and 7 (see Table 1), anisotropic data from sample 18 (Table SI-2), and the K value from quadrupolar splitting values (see Table 2), we found that x_{PBLG}^{pu} is equal to 15 %. From the set of $1/T_{1Z}$ data, we obtained x_{PBLG}^{pu} equal to 16 %. Using x_{PBLG}^{pu} = 15.5 % we found that %w/w value of PBLG is equal to 13.5 %. The good agreement between both values of x_{PBLG}^{pu} validates Eq. SI-12 in predicting the x_{PBLG}^{pu} quantity in the case of a biphasic system involving two chemically different polypeptides. Physically, this result tends to prove the presence of PBLG fibers in the anisotropic regions made mainly of the PCBLL fibers. To support this idea, we have recorded the ^2H spectrum of bza dissolved in 50 mg of PCBLL in 400 mg of chloroform, namely a sample where the w/w concentration in polypeptide is only 10% (sample 20). At this w/w concentration, we obtain a biphasic system containing over 95 % of isotropic phase. This proportion of isotropic phase is much larger than that for the sample 18 (45%), thus showing the role of short PBLG fibers to the formation of anisotropic domains. The conclusion also suggests that in the anisotropic regions, the long fibers of PCBLL orientate the short fibers of PBLG to produce

homogeneous oriented domains. Under this condition, we can re-use the model described for the case of two polymers which form a «neat» liquid-crystalline phase by themselves.

In the isotropic regions of sample 18, the T_{1Z} value (236 ms) also differs from T_{1Z} value measured in «neat» chloroform (T_{1Z} = 538 ms) and in the isotropic region of sample 19 composed only of PBLG with DP = 114 (T_{1Z} = 272 ms). This indicates that different dynamics of the solute in the isotropic regions in these three samples are a result of changes in their respective viscosities. Here again, the presence of PCBLL fibers in the isotropic regions of the sample 18, which mainly contain PBLG fibers of low DP could explain these differences. This situation would modify T_{1Z} even without providing an oriented solvent. Using the T_{1Z} values measured in the «neat» mesophases at 300 K (sample 2 and 7), we can estimate from Eq. 4 (main text) with A = 1/ T_{1Z} that the x^{pu}_{PCBLL} ($x^{pu}_{PCBLL} = 1 - x^{pu}_{PBLG}$) of PCBLL fibers in the isotropic regions is around 33 ± 2%, corresponding to a %w/w value of PCBLL equal to 29 ± 2%. Nevertheless, this proportion of PCBLL in the isotropic regions where PBLG is dominant is insufficient to produce an oriented phase. Finally, to confirm that the origin of the biphasic mesophase in sample 18 is mainly due to the difference in DP, we have prepared a new sample by dissolving 50 mg of bza in 50 mg of PBLG with low DP (DP = 114) and 50 mg of PBLG with high DP (DP = 1352) (sample 21). As it can be seen in Fig. SI-3b we observe a biphasic system with a ratio of 67/33 in favour of the isotropic region (see Table SI-2). The co-existence of isotropic and oriented regions is a consequence of the strong difference in DP of polymers used and is not related to the fact that polypeptides are chemically different. In practice, it is therefore important to use chemically different polypeptides with very similar DP's in order to prevent biphasic samples, a situation not suitable for analytical applications.

Details of the composition of all samples. Details on the sample preparation can be found in the main text.

Table SI-3. Notation and composition of samples prepared in chloroform

Sample	Solute	% in wt PBLG	DP [b] PBLG / PCBLL	Polymer(s) PBLG / PCBLL / mg[c]	Solute / mg[c]	Chloroform / mg[c]	Wt % of polymer
1	bza[a]		- / -	- / -	50	450	-
2	bza[a]	100	1352 / -	101 / -	50	352	20.1
3	bza	86	1352 / 1100	86 / 14	50	352	19,9
4	bza	70	1352 / 1100	70 / 30	50	349	20.0
5	bza[a]	50	1352 / 1100	50 /50	51	351	19,9
6	bza	25	1352 / 1100	25 / 75	50	352	19.9
7	bza[a]]	0	- / 1100	- / 99	51	349	19.9
8	bza[a]	50	782 / 778	50 / 51	50	352	20.7
9	tol	100	782 / 778	100 / 0	51	553	14.2
10	tol	50	782 / 778	51 / 50	50	552	14.3
11	tol	0	782 / 778	0 / 100	51	554	14.2
12	phe	100	782 / 778	99 / 0	50	556	14.1
13	phe	50	782 / 778	50 / 50	49	557	14.2
14	phe	0	782 / 778	0 / 100	50	555	14.2
15	pha	100	782	99 / 0	10	541	15.3
16	pha	50	782 / 778	50 / 50	11	540	15,4
17	pha	0	778	0 / 101	10	542	15.4
18	bza[a]	50	114 / 1100	50 / 50	51	350	20.0
19	bza[a]	100	114 / -	100 / 0	50	349	20.0
20	bza[a]	0	0 / 1100	0 / 51	51	400	10.2

21[d]	bza[a]	100	(114 + 1352) / -	(50 + 49) / 0	49	352	19.8

[a] Benzylic alcohol enriched in ^{13}C in the methylene group. [b] DP : Average degree of polymerization of PBLG and PCBLL used. [c] The accuracy on the weighting is 1 mg. [d] Sample made by mixing two kinds of PBLG fibers with different DPs.

References for the Supplementary Information.

[1] C. Aroulanda, M. Sarfati, J. Courtieu, P. Lesot, *Enantiomer*, **2001**, *6*, 281-287.

[2] C. Canlet, D. Merlet, P. Lesot, A. Meddour, A. Loewenstein, J. Courtieu, *Tetrahedron Asymmetry*, **2000**, *11*, 1911-1918.

[3] a) J. W. Emsley, G. R. Luckhurst, H. S. Sachdev, *Mol. Phys*., **1989**, *67*, 151-160; b) C. Zannoni, In *Nuclear Magnetic Resonance of Liquid Crystals*, pg. 1-34, Reidel, Dordrecht, **1985**.

[4] a) M. H. Levitt In *Spin Dynamics*, Ed. Wiley & sons, Chichester, UK. **2005**; b) C. Boeffel, Z. Luz, R. Poupko, A. J. Vega, *Israel J. Chem.*, **1989**, *28*, 283-296.

[5] J. Prost, P.-G. de Gennes, In *Physics of Liquid Crystals*, Oxford University Press, **1995**.

[6] a) R. L. C. Vink, S. Wolfsheimer, T. Schilling, *J. Chem. Phys*., **2005**, *123*, 074901/1-074901/9; b) W. Chen, D. G. Gray, *Langmuir*, **2002**, *18*, 633-637.