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Chirality in Dynamic Supramolecular Nanotubes Induced by a Chiral Solvent

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Abstract: Amplification of chirality has been reported in polymeric systems. It has also been shown that related effects can occur in polymer-like dynamic supramolecular aggregates, if a subtle balance between noncovalent interactions allows the coupling between a chiral information and a cooperative aggregation process. In this context, we report a strong majority-rules effect in the formation of chiral dynamic nanotubes from chiral bisurea monomers. Furthermore, similar helical nanotubes (with the same circular dichroism signature) can be obtained from racemic monomers in a chiral solvent. Competition experiments reveal the relative strength of the helical bias induced by the chiral monomer or by the chiral solvent. The nanotube handedness is imposed by the monomer chirality, whatever the solvent chirality. However, the chirality of the solvent has a significant effect on the degree of chiral induction.

Keywords: chirality · chiral solvents · nanotubes · self-assembly · supramolecular chemistry

Introduction

The control of chirality amplification is a prominent objective, because understanding how a slight enantiomeric excess in a racemate can be amplified, may help unravel the mystery of the origin of chirality in biological systems. Amplification of chirality is also important for chemistry and materials science, in applications such as enantioselective catalysis and chiral separation or sensing.[1] The amplification of chirality was first studied in polymeric systems and is now a well known phenomenon.[2] More recently, it has been shown that related effects can also occur in polymer-like dynamic supramolecular aggregates,[3] if a subtle balance between noncovalent interactions allows the coupling between a chiral information and a cooperative aggregation process. So far, most studies have dealt with non-linear effects occurring when a chiral monomer is mixed with a non-chiral monomer (sergeants-and-soldiers principle) or with its racemate (majority-rules principle).[3] In contrast, only few studies concern the effect of chiral additives,[4] and even fewer report on the use of chiral solvents.[5–7] However, from a practical point of view, the introduction of chiral information in a dynamic supramolecular aggregate, via a simple chiral solvent instead of an elaborate chiral monomer, is certainly very attractive.

We have recently shown that racemic bisureas **EHUT-*rac*** self-assemble in non polar solvents to form extremely long nanotubes, through a strongly cooperative process.[8] These

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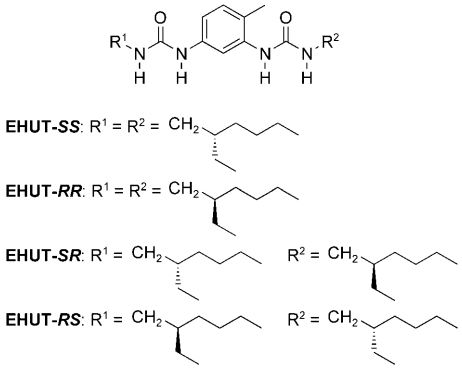
nanotubes are in dynamic exchange with the monomer and with simple hydrogen-bonded filaments.[8a] Moreover they can form only if the solvent molecules are small enough to be accommodated within the tubes, thereby contributing to their stabilization.[8b,e] We therefore considered that this host–guest system was well suited to study the possibility of chirality transfer from the solvent to the supramolecular nanotube. Herein, we report the formation of chiral dynamic nanotubes i) from chiral monomers,[6a,9] or ii) from racemic monomers in a chiral solvent, and iii) the competition between the two processes.

Results and Discussion

Enantio-enriched monomers **EHUT-*SS*** and **EHUT-*RR*** were synthesized from toluene diisocyanate and the corresponding optically pure[10] 2-ethylhexylamines. The optical purity of the monomers was characterized by chiral HPLC: their enantiomeric excess is 78% and 70% respectively (see the Supporting Information). The reference compound **EHUT-*rac*** was obtained by reacting toluene diisocyanate with racemic 2-ethylhexylamine, and therefore contains the four isomers **EHUT-*SS***, **-*RR***, **-*RS*** and **-*SR*** in equimolar amounts (Scheme 1). The first step is to probe the supramolecular structure formed by an enantiopure monomer in comparison to the racemic mixture, because in some cases, chirality has been shown to strongly affect the assembly pattern.[3f,11] Figure S1 and S2 show that the small angle neutron scattering (SANS) curves and the FTIR spectra of **EHUT-*SS*** and **EHUT-*rac*** are identical, proving that the enantio-enriched monomer forms the same supramolecular architecture as the racemic mixture. Moreover, the high cooperativity of the transition between the nanotubes and the filaments affords a sensitive measure of the relative stability of the two structures.[8] This transition occurs at the same temperature for **EHUT-*SS*** and **EHUT-*rac*** (Figure S3), showing that the tube and filament structures are not significantly affected by the chirality of the monomer.



Scheme 1. Structure of bisurea monomers.

Circular dichroism (CD) spectroscopy was then used to investigate further the effect of the chiral side chains. No CD signal is observed for **EHUT-*SS*** in ethanol (data not shown), probably because no supramolecular structure is formed in this strongly interacting solvent, and the chiral centers are too far from the urea and aromatic chromophores. However, in cyclohexane at room temperature, a strong bisignated Cotton effect is observed with a negative and positive maxima at $\lambda = 236$ and 224 nm, respectively (Figure 1). A weak positive band also appears at $\lambda = 290$ nm.

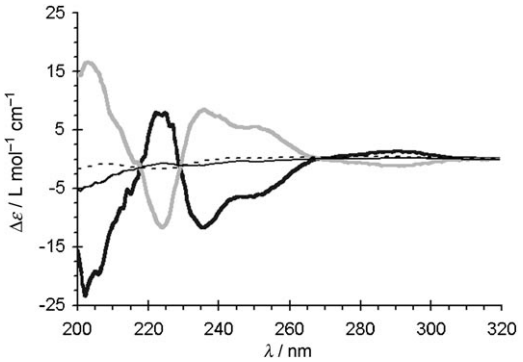


Figure 1. CD spectra of 1 mM solutions in cyclohexane of: a) **EHUT-*SS*** at 20°C (bold black line); b) **EHUT-*RR*** at 20°C (bold grey line); c) **EHUT-*SS*** at 60°C (black line); d) **EHUT-*rac*** at 20°C (dashed black line).

The comparison of this CD signal to the UV/Vis absorption spectrum (Figure S4) suggests that the bisignated Cotton effect may result from an exciton coupling within the self-assembled nanotube. In any case, the opposite CD signal obtained with the mirror image isomer **EHUT-*RR***, and the disappearance of the CD signal at temperatures above the tube-filament transition (51°C) are clear evidence that there is a transfer of chirality from the alkyl side chains of the monomer to the urea and aromatic chromophores within the self-assembled nanotubes.

Mixing enantiomers is a simple method to obtain structural information on a self-assembled system.[3a] Therefore, stock solutions of **EHUT-*SS*** or **EHUT-*RR*** in cyclohexane were combined in different proportions and stirred at room temperature. Figure 2 shows the result of the CD measurements at equilibrium.[12] The highly non-linear variation of the ellipticity is remarkable and shows that an enantiomeric excess of only 10% is sufficient to impose the chiral twist of the majority enantiomer. It also shows that the nanotubes are indeed in dynamic exchange at room temperature, because this chiral amplification can only occur if the assemblies of the pure enantiomers reorganize after mixing. Moreover, this strong majority-rules effect is also observed if solutions of **EHUT-*SS*** and **EHUT-*rac*** are combined in different proportions (Figure 2). This means that the dilution by the other isomers (**EHUT-*SR*** and **EHUT-*RS***) does not destroy the cooperativity of the process. Van Gestel et al. have recently reported a theoretical model, which quantitatively

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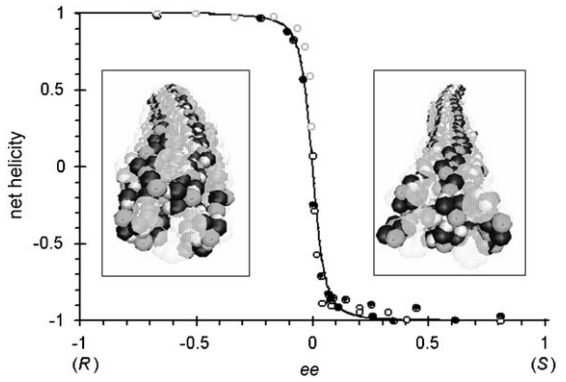

Figure 2. Net helicity ($(\Delta\varepsilon_{236}-\Delta\varepsilon_{224})/(\Delta\varepsilon_{236}-\Delta\varepsilon_{224})_{max}$) versus enantiomeric excess (*ee*) of 1 mM bisurea solutions in cyclohexane at 20 °C, for the following mixtures: **EHUT-*SS*/EHUT-*RR*** (●); **EHUT-*SS*/EHUT-*rac*** (○); **EHUT-*RR*/EHUT-*rac*** (○).The curve is a fit of the **EHUT-*SS*/EHUT-*RR*** data.[13c] The *ee* is calculated as $([S]-[R])/([R]+[S])$, for which $[R]$ and $[S]$ are the ethylhexyl concentrations, as deduced from the measured optical purity of the monomers. The insets show optimized geometries for an **EHUT-*RR*** (left) or **EHUT-*SS*** (right) nanotube, determined by molecular mechanics and dynamics (see Figure S6 for details).

describes chiral amplification effects in one-dimensional self assemblies.[13] They showed that the two relevant parameters for such a system are the energetic penalty for a helix reversal ($\varepsilon_{reversal}$) and the energetic penalty for the presence of a "wrong" enantiomer in an assembly of given helicity ($\varepsilon_{mismatch}$). Following the fitting procedure of van Gestel et al.,[13c,d] it is possible to obtain an excellent agreement with our experimental data (Figure 2) if values of the parameters are $\varepsilon_{reversal} \geq 17\ kJ\,mol^{-1}$ ($=7\ k_BT$) and $\varepsilon_{mismatch} \leq 0.1\ kJ\,mol^{-1}$ ($=0.05\ k_BT$). The very low value for the mismatch penalty is not really surprising and reflects the small energetic destabilization of a (*R*)-ethylhexyl group within a predominantly (*S*)-ethylhexyl domain. Notably, the huge length of the tubes[8d] means that the overall mismatch energy for a given tube can still be significant. Moreover, the large value for a helix reversal penalty is very informative, because it implies that helix reversals are not likely to occur along a nanotube. This in turn means that in racemates, the bisureas tend to self-assemble into a mixture of right-handed or left-handed nanotubes (in adequate proportions), rather than in a kind of multiblock copolymer.[14] Furthermore, the unfavorable interaction between right-handed and left-handed nanotubes indicates a major influence of the chiral side chains on either the hydrogen-bonding pattern or the steric environment of the nanotubes. This last conclusion contradicts the previously reported molecular model for the nanotube for which no twist was visible.[8c] However, the absence of twist was a consequence of the molecular simulation procedure adopted; periodic boundary conditions were imposed to avoid end effects owing to the absence of hydrogen bonding.[15] In the present work, molecular dynamics simulations were performed on long tubes with free extremities, to lift the geometrical constraint imposed by the periodic boundary conditions. With this new procedure, some twisting of the nanotube clearly appears (Figure 2 inset and Figure S6). This improved model is now compatible both with previous experimental data[8c] and with the present CD results.

These results on chiral monomers encouraged us to investigate the effect of a chiral solvent. Limonene was selected because of i) its size which is compatible with the inner space of the nanotubes,[8b] ii) the absence of polar groups which would interfere with self-assembly by hydrogen bonding, and iii) its commercial availability. FTIR and DSC experiments (Figures S7 and S8) confirm that the nanotubes are formed in limonene, with a tube-to-filament transition temperature of 38 °C. Figure 3a shows the symmetrical CD

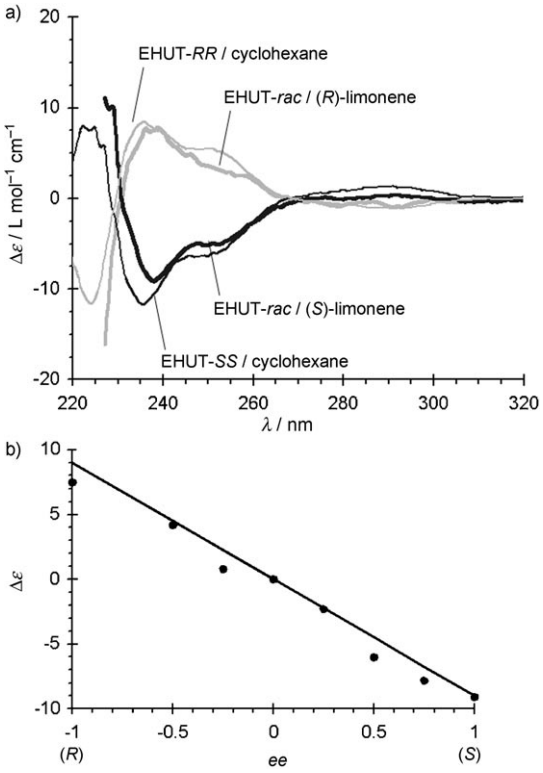

Figure 3. a) CD spectra at 20 °C of bisurea solutions: **EHUT-*rac*** in (*S*)-limonene (black bold line) or (*R*)-limonene (grey bold line) (10 mM); **EHUT-*SS*** (black line) or **EHUT-*RR*** (grey line) in cyclohexane (1 mM).[16] b) Helicity measured at $\lambda = 238$ nm versus the enantiomeric excess of **EHUT-*rac*** in (*S*)-limonene/(*R*)-limonene mixtures.[16]

spectra measured for **EHUT-*rac*** solutions in (*S*)- or (*R*)-limonene. The Cotton effects obtained for **EHUT-*rac*** in (*S*)-limonene and **EHUT-*SS*** in cyclohexane have nearly identical shapes: it indicates that the nanotubes formed by the racemic monomer mixture in the chiral solvent and the chiral monomer in the achiral solvent have very similar structures. Moreover, the handedness of the helical assembly is the same whether it is induced by the (*S*)-limonene solvent or by the **EHUT-*SS*** monomer. Now, this raises the question of whether the chiral induction by the solvent is quantitative (like the chiral induction by the monomer) or only partial. The fact that the signal intensities in the CD

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spectra of Figure 3a are very similar does not necessarily mean that full chiral induction is achieved by chiral limonene, because the CD signal intensity is known to also depend on the solvent polarizability.[17]

To address this question, we performed the following experiment. Stock solutions of **EHUT-*rac*** in (*S*)- or (*R*)-limonene were combined in different proportions and stirred at room temperature. Figure 3b shows the result of the CD measurements at equilibrium; the ellipticity is a linear function of the solvent enantiomeric excess. This points to a very different behavior (and energetics) when the helicity of the nanotubes is biased through a chiral solvent or through a chiral monomer. However, we still do not know if full chiral induction is induced by the solvent, because no saturation of the helicity is reached.[13c]

Finally, the respective magnitude of the nanotube helicity control by a chiral monomer or by a chiral solvent was probed through the following competition experiments. Figure 4 shows the results of the four possible combinations

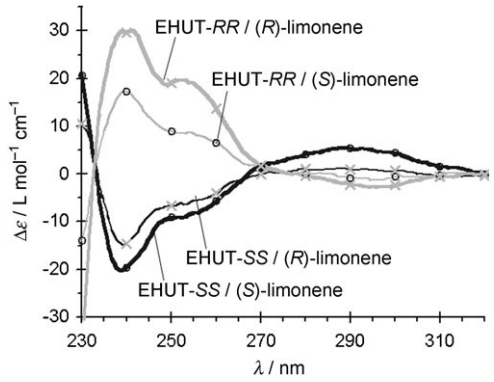

Figure 4. CD spectra at 20 °C of 10 mM bisurea solutions: **EHUT-*SS*** in (*S*)-limonene (——●——); **EHUT-*SS*** in (*R*)-limonene (——×——); **EHUT-*RR*** in (*R*)-limonene (——×——); **EHUT-*RR*** in (*S*)-limonene (——○——).

between the two chiral monomers and the two chiral solvents. Clearly, the handedness of the nanotube is imposed by the monomer because the Cotton effect is of the same sign for **EHUT-*RR*** in both (*S*)- and (*R*)-limonene. However, the intensity difference between these two spectra confirms the significant effect of the solvent. It is reasonable to assume that full chiral induction is reached for **EHUT-*RR*** in (*R*)-limonene, because this is already the case in cyclohexane (Figure 2). Therefore, the intensity of the Cotton effect for this system ($\Delta\varepsilon = 24.5\ L\,mol^{-1}\,cm^{-1}$, Figure 4)[18] can be used to normalize the value obtained in the case of **EHUT-*rac*** in (*R*)-limonene ($\Delta\varepsilon = 8.3\ L\,mol^{-1}\,cm^{-1}$, Figure 3a): this yields a value of 33% for the chiral induction by the chiral solvent. Although full chirality induction by the solvent alone is not reached, this value is quite significant.

Moreover, this value can now be used to determine the energetic parameters relevant for this chiral induction by the solvent. Although the theoretical model devised by van Gestel et al. was formally written for the case of a mixture of chiral monomers, it is equally valid for the present case of a one-dimensional assembly for which helicity is controlled by a chiral solvent. The lack of cooperativity of the experimental curve (Figure 3b) does not enable to determine both parameters $\varepsilon_{reversal}$ and $\varepsilon_{mismatch}$ independently. However, we can assume that the helix reversal penalty depends mainly on the hydrogen bonding pattern of the nanotube and therefore not much on the solvent. If the previously determined minimum value of $\varepsilon_{reversal}$ is used ($17\ kJ\,mol^{-1}$), then a value $\varepsilon_{mismatch} = 1.5\ J\,mol^{-1}$ ($= 0.0006\ kT$) affords a good fit of the data (Figure S9). Although this value is quite low, it is not unrealistic. Even lower values have been found in the case of chiral solvation for helical polymers.[2]

Conclusions

In conclusion, we have shown for the first time that chiral dynamic self-assembled nanotubes can be obtained from a racemic monomer in a chiral solvent. The helical bias induced by the particular solvent tested (limonene) is not as strong as the helical bias induced by a chiral monomer, but is still very significant (about 33%). These results do not allow us to determine if the solvent control on the nanotube helicity is affected by the limonene molecules present within the nanotube or outside or both. However, it is tempting to assume that a host–guest type of interaction is operative, because it should be stronger than simple solvation. Finally, it is therefore not unreasonable to expect that a better chiral guest can be found, which will induce a full helical bias of the nanotubes.

Acknowledgements

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[14] The observed majority-rule effect implies that the nanotubes are not made from a single enantiomer, but contain a mixture of enantiomers: the major enantiomer in a given nanotube imposes the helicity of this nanotube.

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[16] Because the UV absorption of limonene is higher than that of cyclohexane, the pathlength of the cell for CD measurement had to be reduced, and consequently, the bisurea concentration had to be increased in limonene (see the Supporting Information).

[17] *Biophysical chemistry*, Part II (Ed.: C. R. Cantor, P. R. Schimmel), W. H. Freeman & Co, New York, **1998**.

[18] This value is the average between **EHUT-*RR*** and **EHUT-*SS*** data. The difference between both data is due to the difficulty to precisely control the pathlength of the very thin cell (0.001 cm).

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