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# Bulkiness as a design element to increase the rigidity and macrodipole of supramolecular polymers

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## ABSTRACT

*N,N'*-dialkyl ureas in non-polar solvents self-assemble as hydrogen bonded chains. Infrared and dielectric spectroscopy show that more sterically crowded monomers form shorter chains but also larger macrodipoles. This unexpected effect is due to the enhanced rigidity of the bulky assemblies, as confirmed by molecular dynamics simulations.

Molecular systems with large macrodipoles are useful in numerous fields such as responsive materials (that display piezo-, pyro- or ferroelectricity),<sup>1</sup> directional electron<sup>2</sup> or ion transport (with membrane proteins<sup>3</sup> or synthetic transporters<sup>4</sup>) or catalysis (where long-range macrodipole-ion interactions can help stabilize reactive intermediates<sup>5,6</sup>). In this context, supramolecular polymers (*i.e.*, linear and reversible assemblies of monomers) are of particular interest because of their synthetic accessibility, tunability and responsiveness.<sup>7</sup> To create a large macrodipole by assembly of polar monomers, it is essential to obtain a rigid final assembly, and the overwhelming approach to enforce rigidity is to use multiple point attachments between the monomers, such as multiple hydrogen bonds in benzene-tricarboxamides<sup>8-14</sup> or cyclohexane-tricarboxamides.<sup>15,16</sup>

When the monomers are held by strong covalent bonds, steric hindrance between the repeat units is a straightforward approach to impart rigidity to the resulting polymer.<sup>17,18</sup> Although intermolecular steric hindrance can probably also be expected to favour rigidity in supramolecular polymers, this simple concept has been completely neglected,<sup>‡</sup> probably because of the obvious detrimental effect on the size of the assemblies.<sup>19</sup>

However, we now demonstrate that increasing intermolecular steric interactions between the monomers can actually result in assemblies with a significantly larger dipole moment, because the effect on the size is more than compensated by the effect on the rigidity of the assemblies.

*sym*-Dialkyl ureas (Chart 1) dissolved in non-polar solvents self-associate as hydrogen-bonded chains, as a direct consequence of the trans-trans conformation of the ureido moiety.<sup>20-22</sup> The formation of such macrodipoles is responsible for an increased dielectric constant of the solution.<sup>23</sup> For a given molecule, it is well-known that self-association is favoured by an increase in concentration or by a decrease in temperature.<sup>21</sup> Moreover, increasing the size of the urea substituents disfavours the formation of the

assemblies, and leads to shorter chains.<sup>21</sup> In particular, IR spectroscopy measurements show that bulky dialkyl urea **MPHU** forms chains that are two to three times shorter than reference diethyl urea **DEU** (Fig. S1 and S2). *sym*-Dialkyl ureas are characterized by a significant monomer dipole, and the ordered placement of the monomer dipoles along the chains is responsible for the build-up of a large macrodipole.<sup>20</sup> Therefore one would expect longer chains to yield larger macrodipoles and thus a higher static permittivity of the solution.<sup>23</sup> However, dielectric spectroscopy measurements show that a solution of the bulky dialkyl urea (**MPHU**) is more polar than a solution of the reference diethyl urea (**DEU**, which actually forms the longest chains) (Fig. 1). This unexpected effect is quite significant: the static permittivity of the **MPHU** solution is about 50% higher than the value measured for **DEU** (at a mole fraction  $x = 0.04$  and a temperature of 25°C).

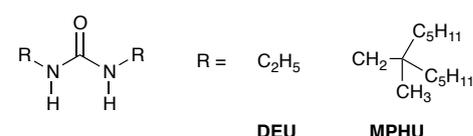
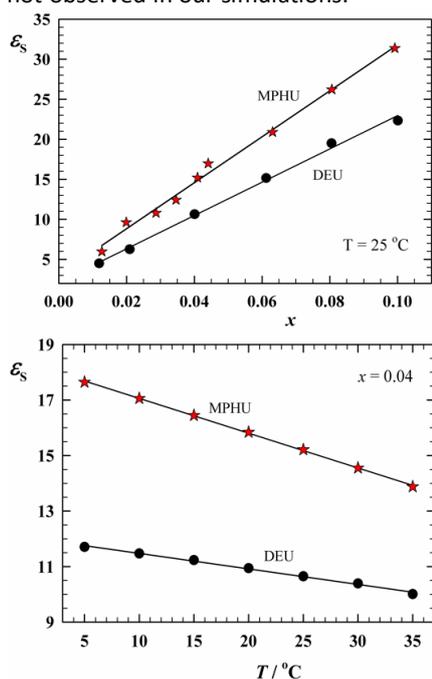


Chart 1

To investigate the reasons for this effect, the conformation and the macrodipole of the chains were probed by molecular dynamics simulations. Starting from a solution of randomly dispersed monomers in an explicit solvent box (urea mole fraction  $x = 0.01$ ), spontaneous aggregation took place for both solutes. After equilibrium, the average chain size was  $8.9 \pm 1.4$  for **DEU** and  $1.4 \pm 0.1$  for **MPHU** (*i.e.*, a larger fraction of **MPHU** molecules were in monomer state instead of forming chains). These figures agree qualitatively with the expected tendency of the monomers with the smallest substituents to form longer chains, but they are smaller than the values deduced from experiment (Fig. S2). This discrepancy can be due to the

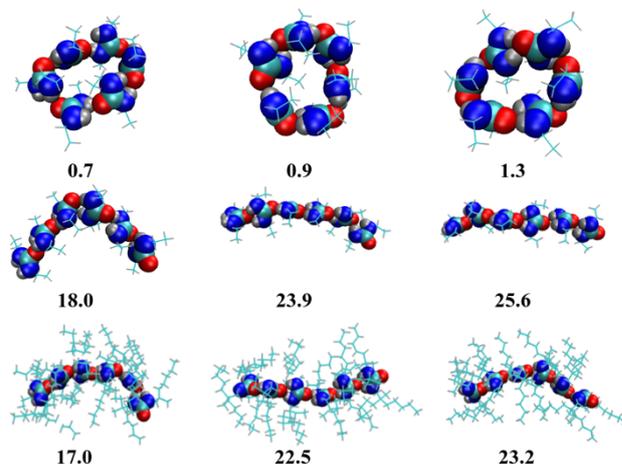
limited size of the simulation system. Besides the size of the chains, the most striking difference between both systems is the presence of cyclic structures in the case of **DEU**. Although cyclic supramolecular polymers are known to form when the repeat unit contains a flexible spacer,<sup>24,25</sup> to the best of our knowledge, there is no previous experimental or theoretical work suggesting the formation of cyclic structures for dialkyl urea supramolecular polymers. In the case of **MPHU**, due to the larger steric hindrance of alkyl groups, the formation of cyclic structures is apparently inhibited, at least for small chain sizes, and was not observed in our simulations.



**Fig. 1** Concentration (top) and temperature dependence (bottom) of the static permittivity of **DEU** and **MPHU** solutions in  $\text{CCl}_4$ . The average size of the hydrogen-bonded chains is known to increase with the molar fraction ( $x$ ) and decrease with the temperature ( $T$ ).<sup>21</sup> See also Fig. S3 for the effect of temperature on the size of the assemblies.

It is instructive to look at some structures with the same chain size sampled from both simulations (and the corresponding macrodipole values) (Fig. 2). The average dipole moment of a monomer in our model is 4.4 D for **DEU** and 4.1 D for **MPHU**. In a hexamer, if the six units were perfectly aligned, the macrodipole would be 26.4 or 24.6 D, respectively. However, due to bends in the chain, the monomer dipoles can partially cancel each other out and the resulting macrodipole were actually smaller than these values. Noticeably, for **DEU** we can find both open and cyclic structures for  $N=6$ , and whenever a cycle is formed the dipoles of the monomers cancel each other out almost completely and the resulting macrodipole is even smaller than the dipole of a single monomer (Fig. 2, top). For **MPHU**, the formation of  $N=6$  cycles is not possible due to the steric hindrance of the aliphatic chains. Taking the open structures

into account, the more bended the structure, the smaller the macrodipole will be. As **MPHU** presents a greater resistance to deformations, the average macrodipole of **MPHU** chains, especially for  $N>3$ , is greater than for **DEU** chains of the same size. For larger chain sizes, the complexity of the chains increases and multiple bends can take place simultaneously, but this general remark is still valid.

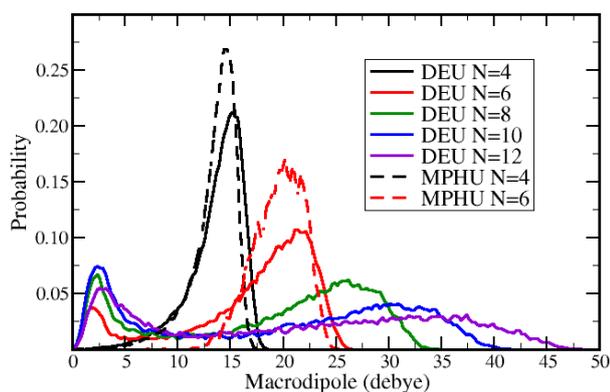


**Fig. 2** Selected structures of hexamers formed in the simulations with the respective dipole moments in debye (D). Top: Cyclic structures of **DEU**; middle: open structures of **DEU**; bottom: open structures of **MPHU**. The urea groups are represented as van der Waals spheres while the aliphatic groups are represented as lines. Atoms: Silver – H, Cyan – C, Dark Blue – N, Red – O.

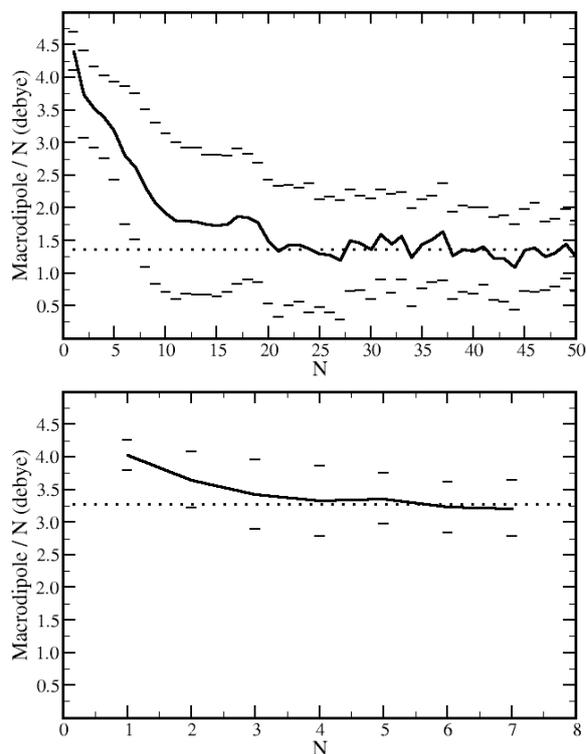
A more quantitative comparison between both solutes can be made by considering the distribution of all macrodipole values for various chain sizes (Fig. 3) instead of looking at the values for arbitrarily chosen structures. For  $N=4$ , both **DEU** and **MPHU** present a single population (*i.e.*, no cycles) but the distribution for **DEU** is more spread, especially with a longer tail at small macrodipole values, due to its greater flexibility. For  $N=6$ , the formation of cycles takes place for **DEU** and the distribution of macrodipoles presents two populations. The main distribution has a maximum at *ca.* 20 D, and corresponds to open chains, whereas a minor population with macrodipoles smaller than 5 D corresponds to the cycles. There is no abrupt transition between both populations since **DEU** chains can be open and yet almost as bended as in a cycle. On the other hand, **MPHU** presents a single population for  $N=6$ , since the steric hindrance renders the chains too rigid to form cycles. This population also has a maximum at *ca.* 20 D but it is less spread than the one of **DEU**, especially on the small dipole side. In summary, both structural patterns must contribute to the different dielectric properties of the solutions of **DEU** and **MPHU**. Only **DEU** can form cycles with almost zero dipole moment, which have a very small contribution to the dielectric constant of the medium, while among open chains, those formed by **DEU** are more likely to bend into smaller macrodipole structures than those formed by **MPHU**.

The sampling for chains longer than 6 monomers was very limited for **MPHU** and hence only the results for **DEU** are shown in Fig. 3 for larger aggregates. For  $N > 6$ , the formation of cycles is even more favourable and, despite the maximum of the open chain population being continuously displaced toward larger macrodipoles as the chain size increases, the distribution also becomes broader due to the increase in the possible number of conformations of the chain. This is an entropic effect: the perfect alignment of monomers that results in the largest macrodipole is only one among all possible conformational states of the chain and the total number of states increases as the chain becomes longer. Cycles were found even for chains as large as 30 **DEU** units, leading to a low macrodipole population within the overall distribution, although a clear separation between the “closed” and “open” chains populations was not discernible (Figures S4 and S5 in Supporting Information).

The average macrodipoles for a chain of size  $N$  was computed and divided by  $N$  (Fig. 4) and corresponds to the average contribution of each repeat unit to the total dipole moment of a chain of size  $N$ . Despite the increase of the macrodipole with the chain size, the contribution per monomer decreases as  $N$  increases until it reaches some plateau, due to the partial cancellation of their individual dipoles. This plateau is reached only at *ca.*  $N=20$  for **DEU** while for **MPHU**, due to the rigidity of the chains, it is reached already for  $N=3$ . For larger chains, the average contribution of each molecule is 1.4 D for **DEU** and 3.3 D for **MPHU**. For **DEU**, this value is more than 3 times lower than the monomer dipole moment (4.4 D). Even for **MPHU** the contribution per molecule is smaller than the monomer dipole moment (4.1 D), indicating some degree of disorder in the alignment of units, but much less than for **DEU**, for which the greater flexibility of the chains and the possibility of cycle formation leads to a greater decrease of the dipole moment as the chain increases.



**Fig. 3** Distribution of macrodipoles for selected cluster sizes for **DEU** (solid lines) and **MPHU** (dashed lines).



**Fig. 4** Average macrodipole per monomer as a function of the polymer size (continuous black line). The dotted line is the average after the plateau is reached ( $N > 20$  for **DEU** and  $N > 3$  for **MPHU**). The horizontal bars stand for the value of the average  $\pm$  the standard deviation. Top: **DEU**, bottom: **MPHU**. See also the analyses in different time windows of the simulation in Fig. S6, which demonstrated the convergence of the simulations and the significance of the data.

In conclusion, increasing the steric bulkiness of a monomer will certainly result in shorter supramolecular assemblies, but will also constrain their conformations. The macrodipole is a quantity that is affected by both effects, and we show that the latter can overwhelm the former. This fact should be taken into account while designing new supramolecular polymers with a large macrodipole for electric field responsiveness, transport phenomena or catalysis.

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the research results reported within this paper. URL: <http://sdumont.lncc.br>.

## Notes and references

‡ Intermolecular steric hindrance in supramolecular polymers has been exploited to avoid lateral aggregation<sup>26</sup> or to favour alternated copolymers from two monomers of differing bulkiness.<sup>27</sup> Steric hindrance is also well-known to allow internal conformational control of the monomers by constraining dihedral angles.<sup>28,29</sup>

§ In the case of **DEU**, the discrepancy is also due to the cyclic structures that were found in the simulations, but not taken into account in the modelling of the IR experimental data.

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