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Aromatic polyimides comprise a class of polymers known as "high performance" due to their high T_g (normally above 200 °C) and thermal stability [1,2]. The imide group in this class of polymers is a five- or six-membered ring. The literature reports very distinct synthetic reaction conditions for these two kinds of aromatic polyimides [1] and the reason for these different synthetic conditions is commonly considered to be a higher stability of the six-membered ring anhydride, in comparison to the five-member ones (Figure 1) [3,4]. Nevertheless, no detailed discussion on the reactivity of these monomers is reported in the literature.





(b)

Figure 1: Six- (NTDA, a) and five-membered (PMDA, b) cyclic anhydrides studied.

The present work reports the investigation on the first and most critical step of the synthesis of aromatic polyimides, namely the formation of polyamic acid (Figure 2), by the use of density functional theory (DFT, BP86-D3(BJ)/def2-TZVP/SMD [5–11], using the ORCA package, version 3.0.2 [12]). Two reaction pathways, (a) and (b), between aniline and either naphthalic tetracarboxylic dianhydride (NTDA, Figure 1a) or pyromellitic anhydride (PMDA, Figure 1b) were considered (Figures 2a and 2b). While (a) is a single step process (Figure 2a), (b) passes through an intermediate (Figure 2b). Energies of the reactants, transition states, intermediates and products were calculated and the reactions were compared in regard of kinetic parameters.

It was shown that, although (a) was the fastest pathway found, its reverse reaction is even faster, and (b) might actually occur. In the gas phase, the rate constant of (a) is around five orders of magnitude higher for PMDA when compared to NTDA. Pathway (b) has comparable magnitude for both substrates, but is 10⁴ slower than (a).

Solvent plays a major role in this process, as shown by implicit solvation in THF, DMF, DMSO and propylene carbonate (PC). For pathway (a), for instance, PMDA reacts 5.1, 71.6, 407.3 and $6.7 \cdot 10^{12}$ times faster in THF, PC, DMF, and DMSO, respectively, than in vacuum. DMSO shows the largest velocity increase for NTDA as well, but it was found to be only 13 faster than in vacuum in this case. Pathway (b) also depended on solvation, although to a smaller degree than (a).



Figure 2: Reaction pathways (a) and (b) employed in this study, here exemplified with PMDA only, for brevity. (a) is a single step process, (b) passes through an intermediate.

We accessed the differences in reactivity between five-membered (PMDA) and six-membered (NTDA) ring anhydrides towards condensation by the use of a homodesmotic reaction (Figure 3), which measured the five-membered ring tension of PMDA to be 3.4 kcal/mol higher than NTDA, in agreement with the prediction of faster reactions promoted by PMDA.



Figure 3: Homodesmotic reaction employed to estimate ring tension, here exemplified with NTDA only, for brevity.

Key-words: polyimides, density functional theory, reaction mechanism. **References:**

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