

*Supplementary Information*

**Heteroaromatic polyamides with improved thermal and mechanical properties**

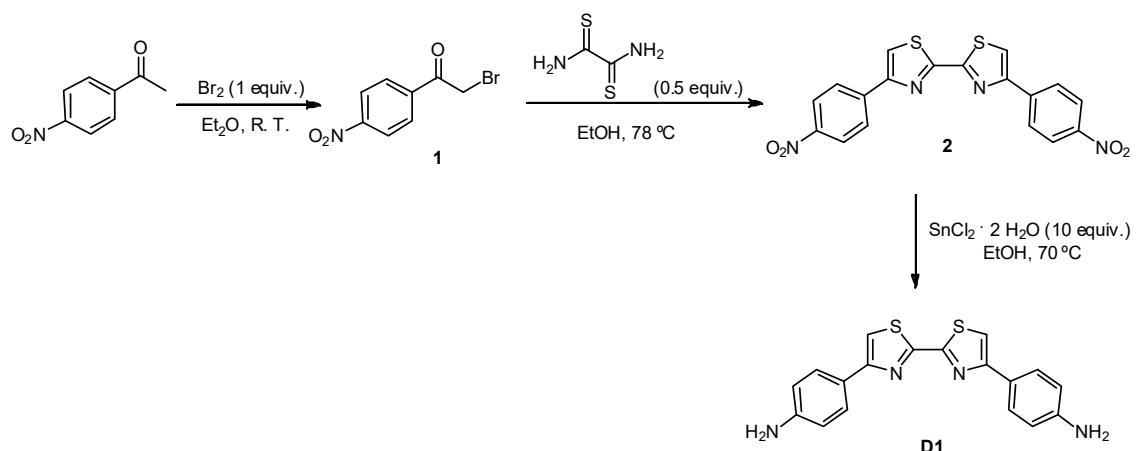
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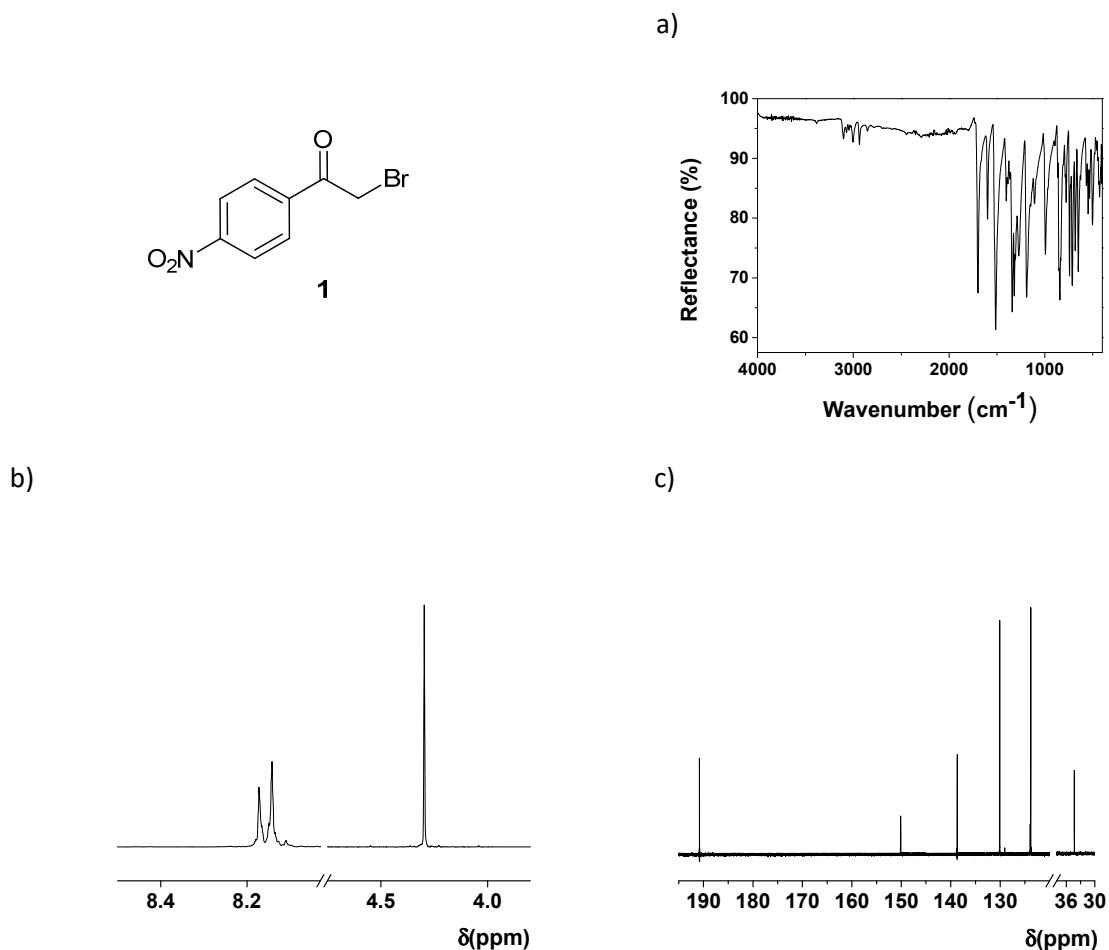
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## S1. Synthesis and characterization of diamine D1 and intermediates

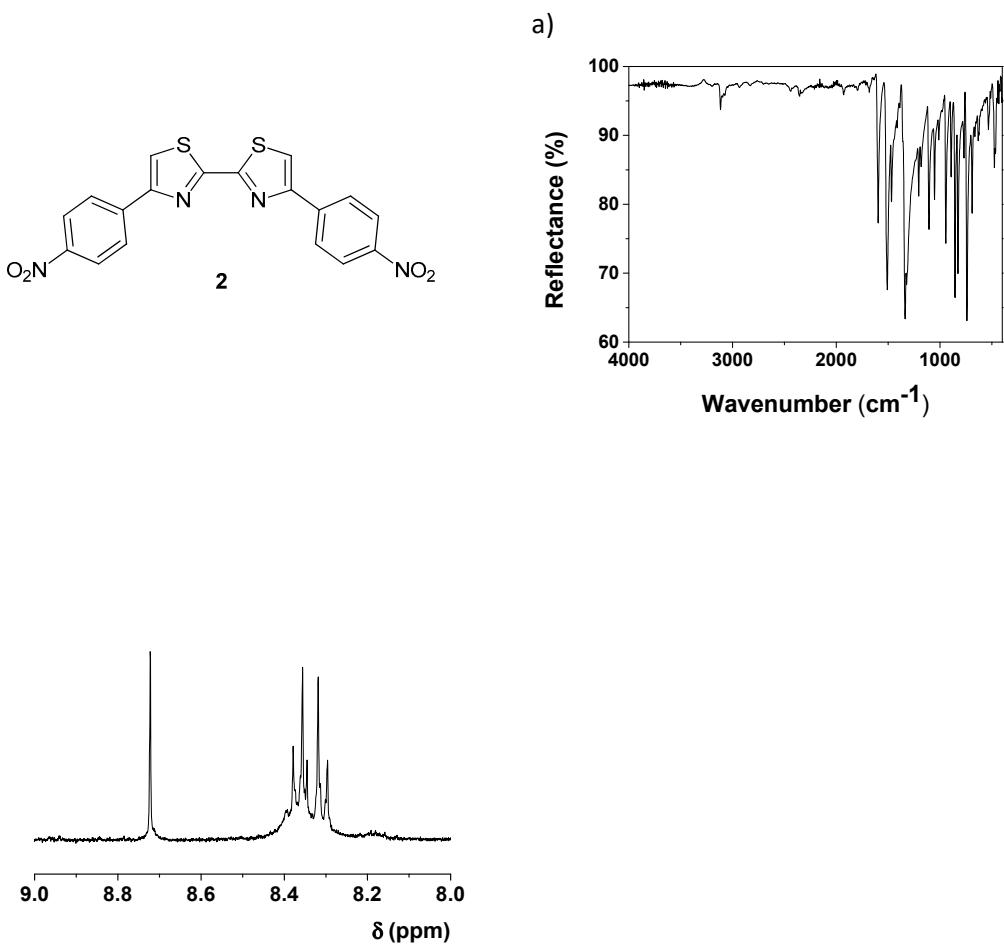


**Characterization of 2-bromo-1-(4-nitrophenyl)ethan-1-one (**1**):**



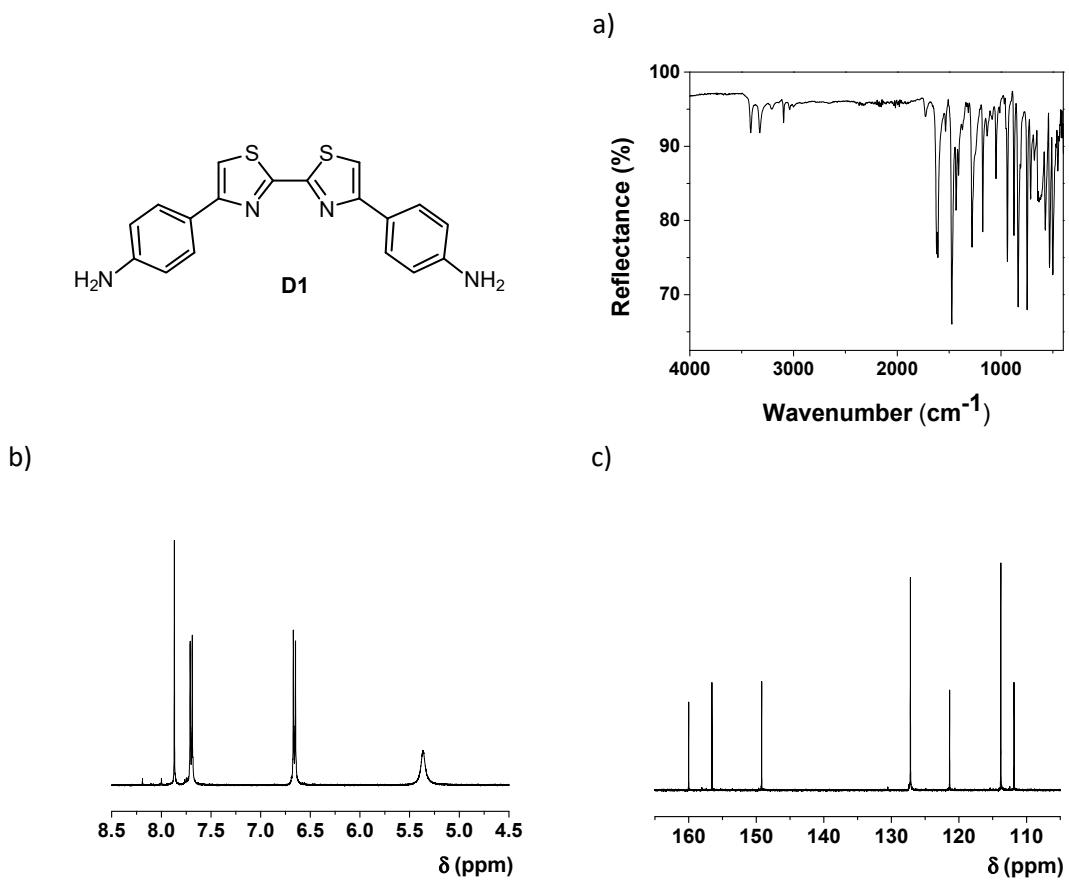
**Figure S1.** Characterization of **1** by (a) FTIR, (b)  $^1\text{H}$  NMR, and (c)  $^{13}\text{C}$  NMR.

**Characterization of 4,4'-bis(4-nitrophenyl)-2,2'-bithiazole (2):**



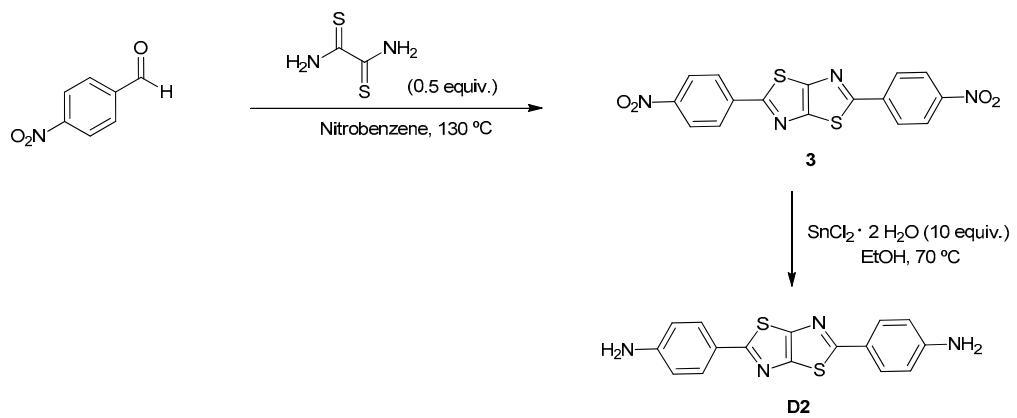
**Figure S2.** Characterization of **2** by (a) FTIR, (b) <sup>1</sup>H NMR.

**Characterization of the monomer 4,4'-([2,2'-bithiazole]-4,4'diyI)dianiline (D1):**

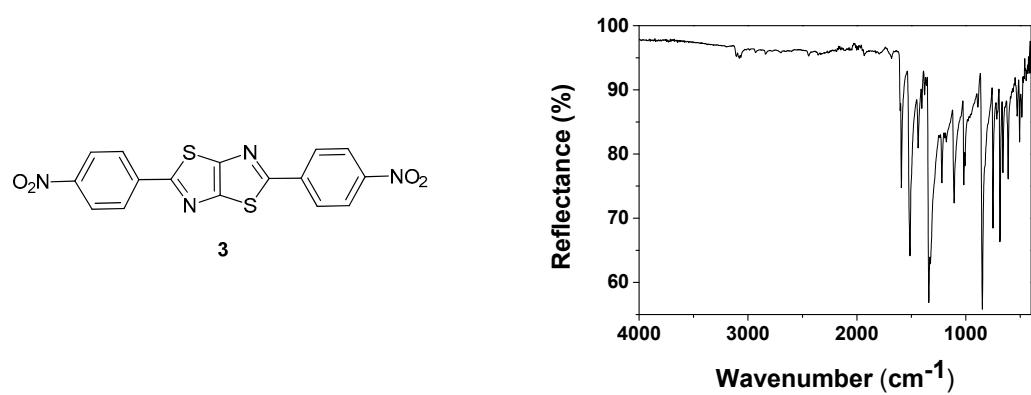


**Figure S3.** Characterization of **D1** by (a) FTIR, (b)  $^1\text{H}$  NMR, and (c)  $^{13}\text{C}$  NMR.

## S2. Characterization of diamine **D2** and intermediate

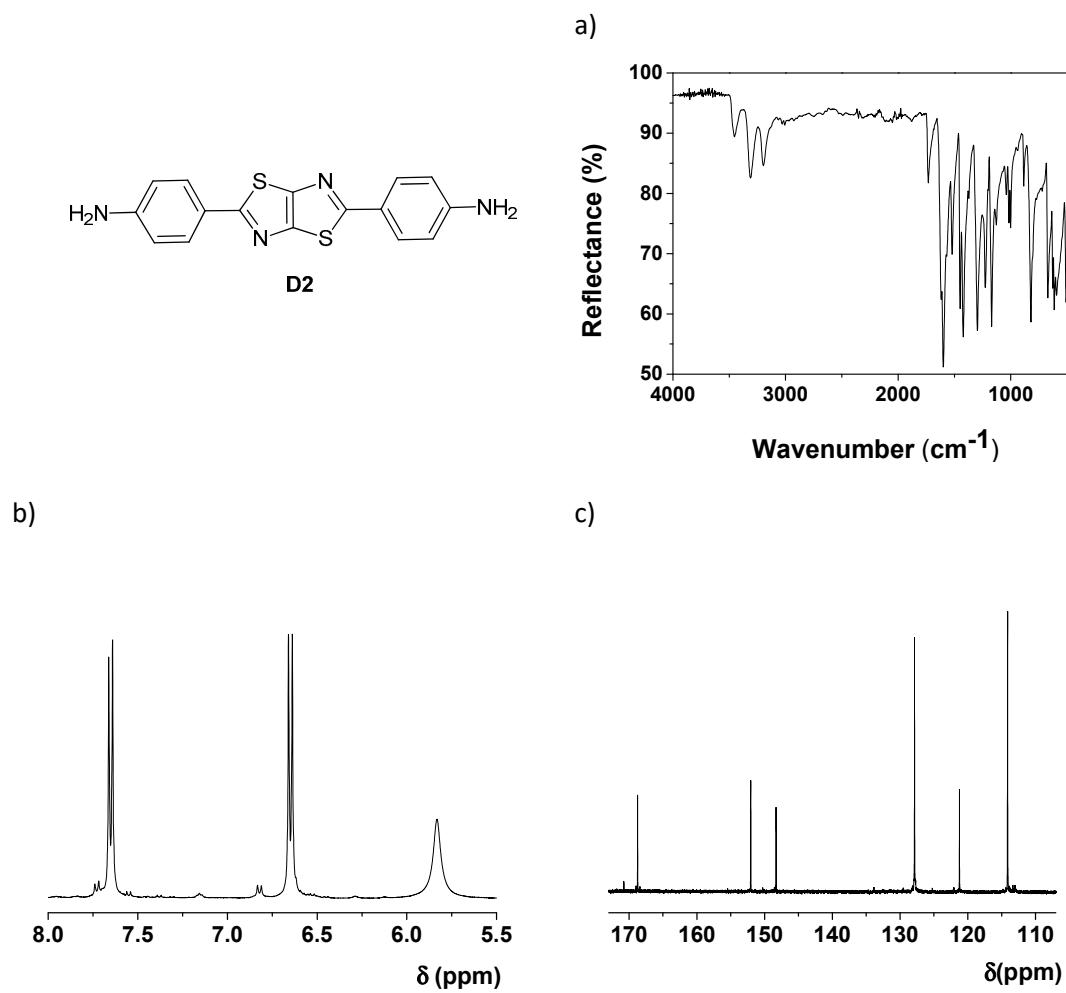


**Characterization of 2,5-bis(4-nitrophenyl)thiazolo[5,4-d]thiazole (3):**



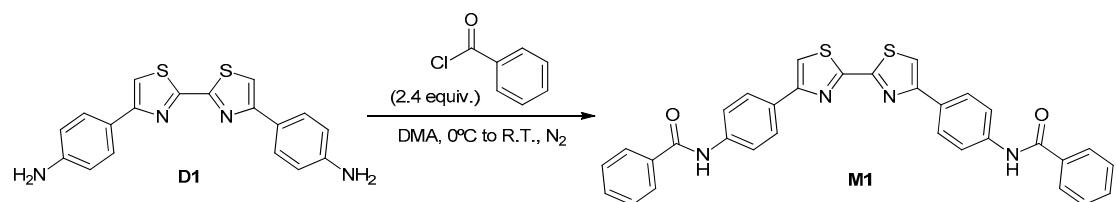
**Figure S4.** Characterization of **3** by FTIR.

**Characterization of the monomer 4,4'-(thiazolo[5,4-d]thiazole-2,5-diyl)dianiline (D2):**



**Figure S5.** Characterization of **D2** by (a) FTIR, (b)  $^1\text{H}$  NMR, and (c)  $^{13}\text{C}$  NMR.

### S3. Characterization of model polyamide M1



**Characterization of *N,N'*-([2,2'-bithiazole]-4,4'diylbis(4,1-phenylene)dibenzamide (M1):**

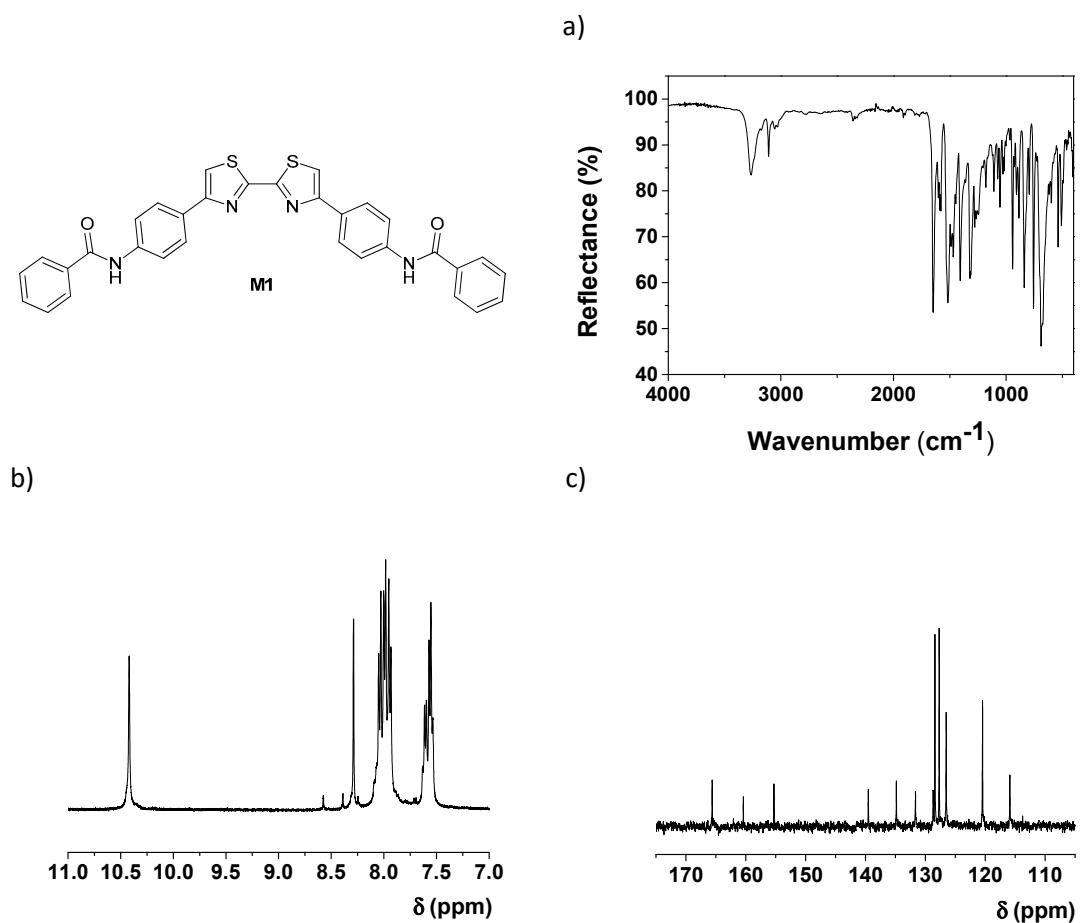
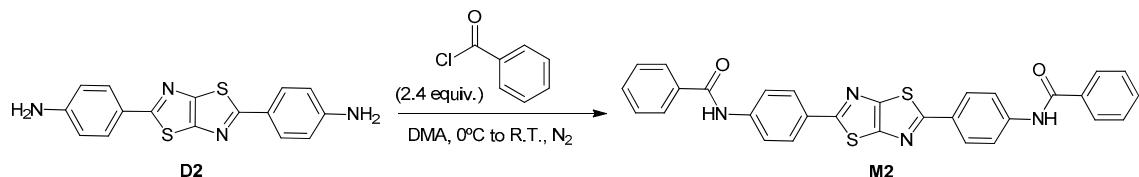
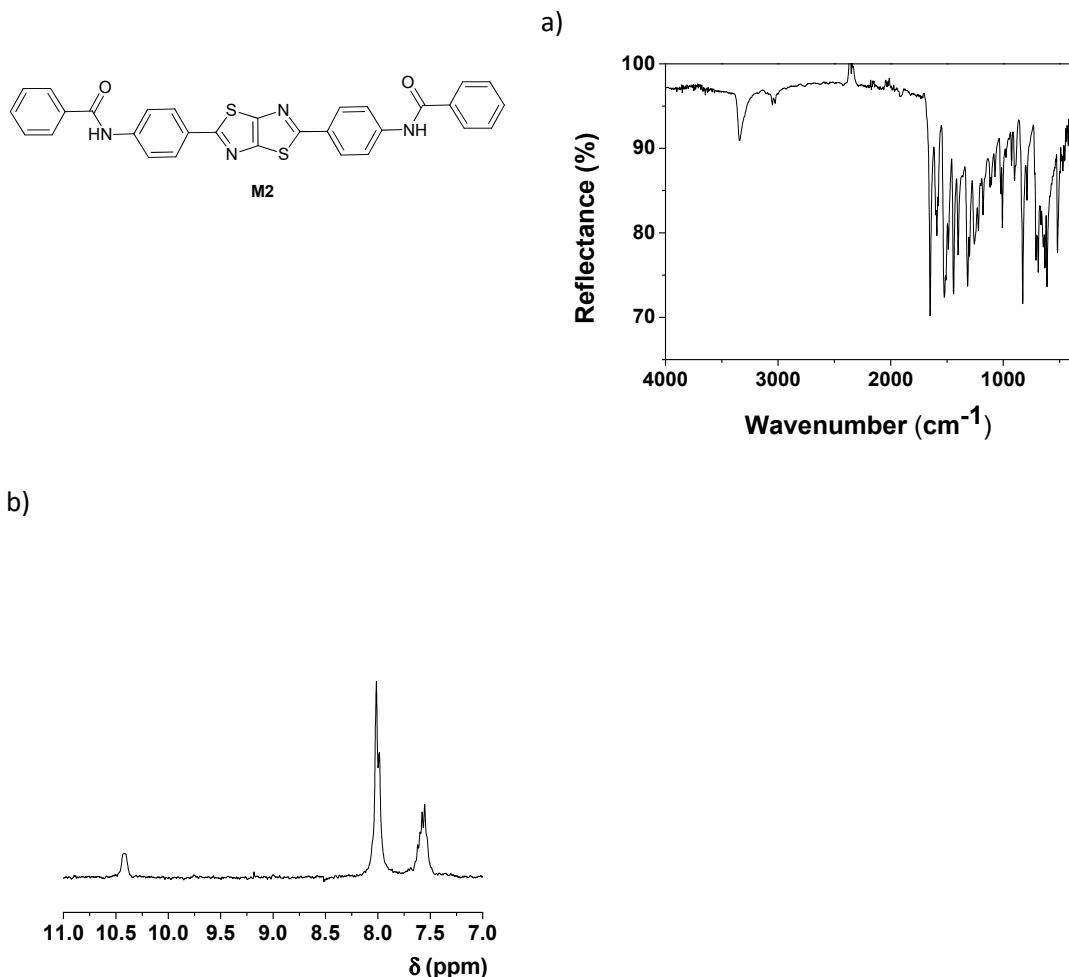


Figure S6. Characterization of M1 by (a) FTIR, (b)  $^1\text{H}$  NMR, and (c)  $^{13}\text{C}$  NMR.

### S4. Characterization of model polyamide M2



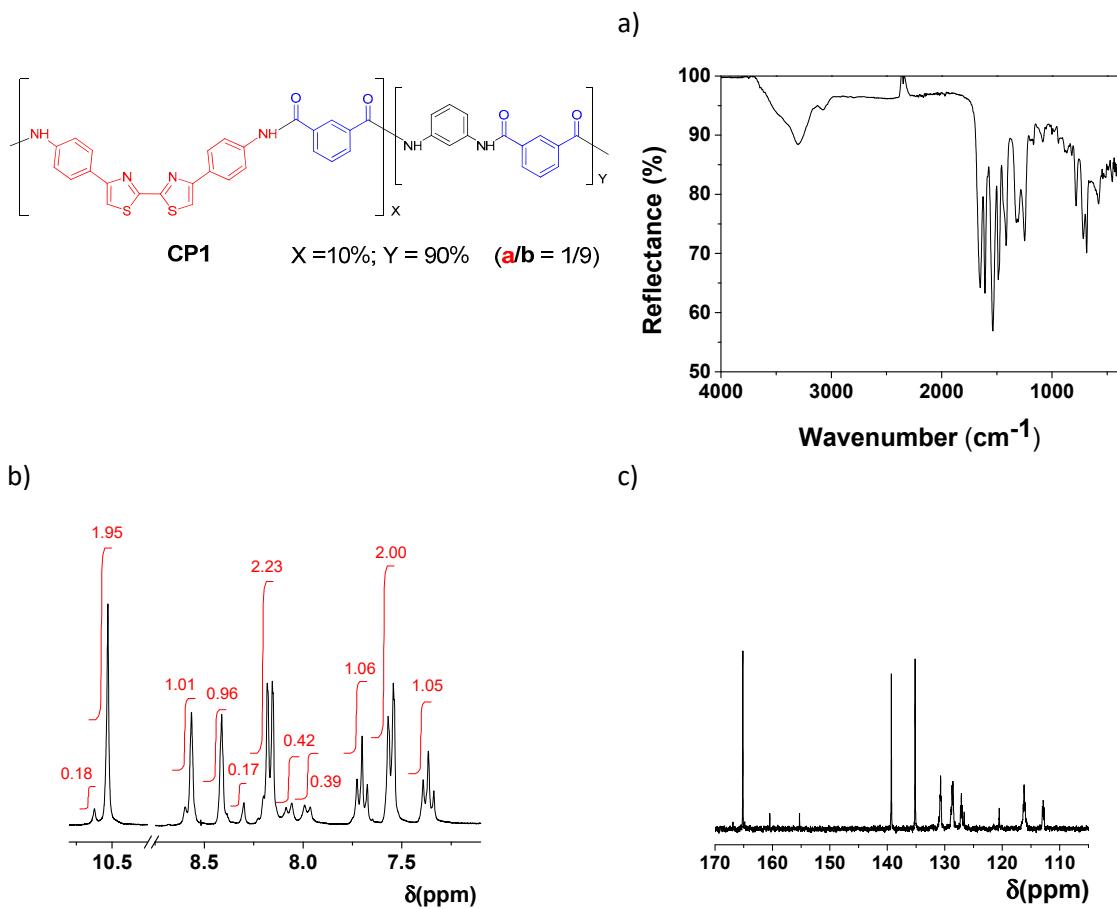
**Characterization of *N,N'*-(thiazolo[5,4-d]thiazole-2,5-diylbis(4,1-phenylene)) dibenzamide (M2):**



**Figure S7.** Characterization of **M2** by (a) FTIR, (b)  $^1\text{H}$  NMR.

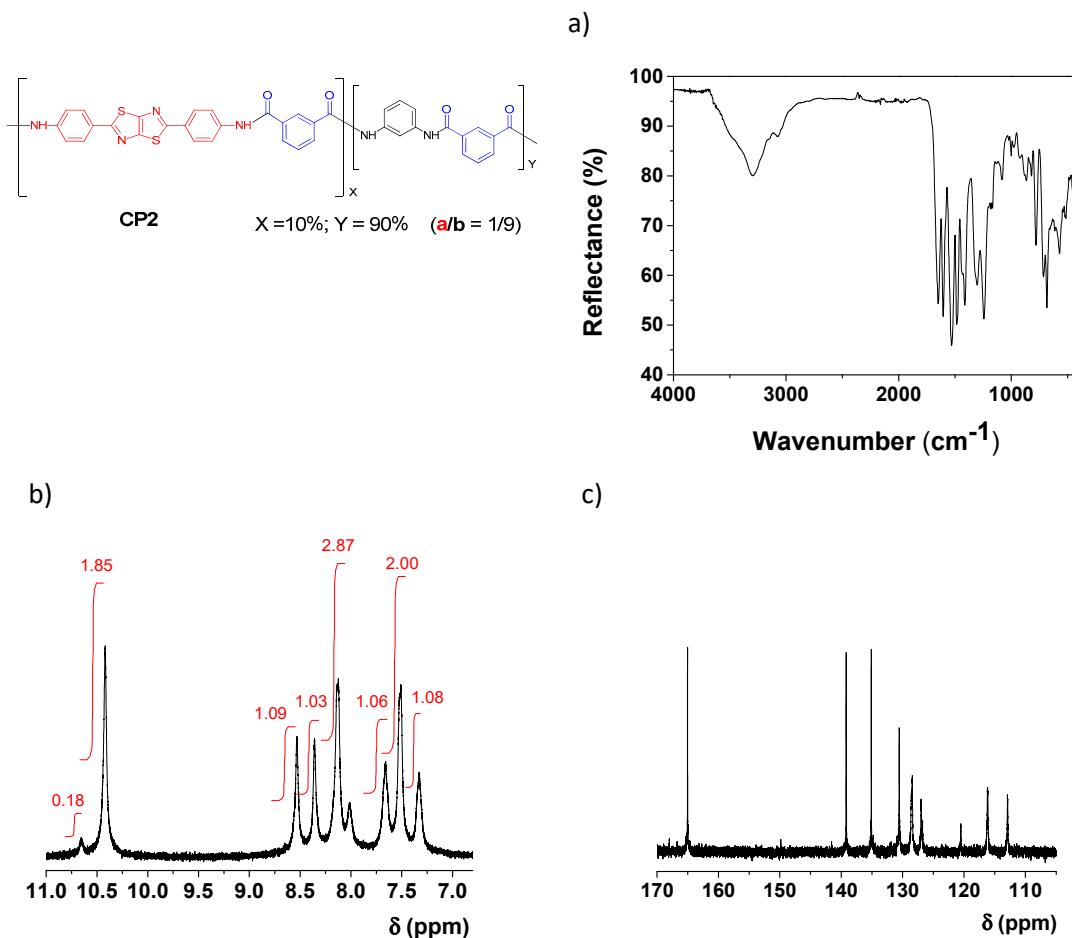
**S5. Characterization of copolymers CP1 and CP2**

**Characterization of CP1:**



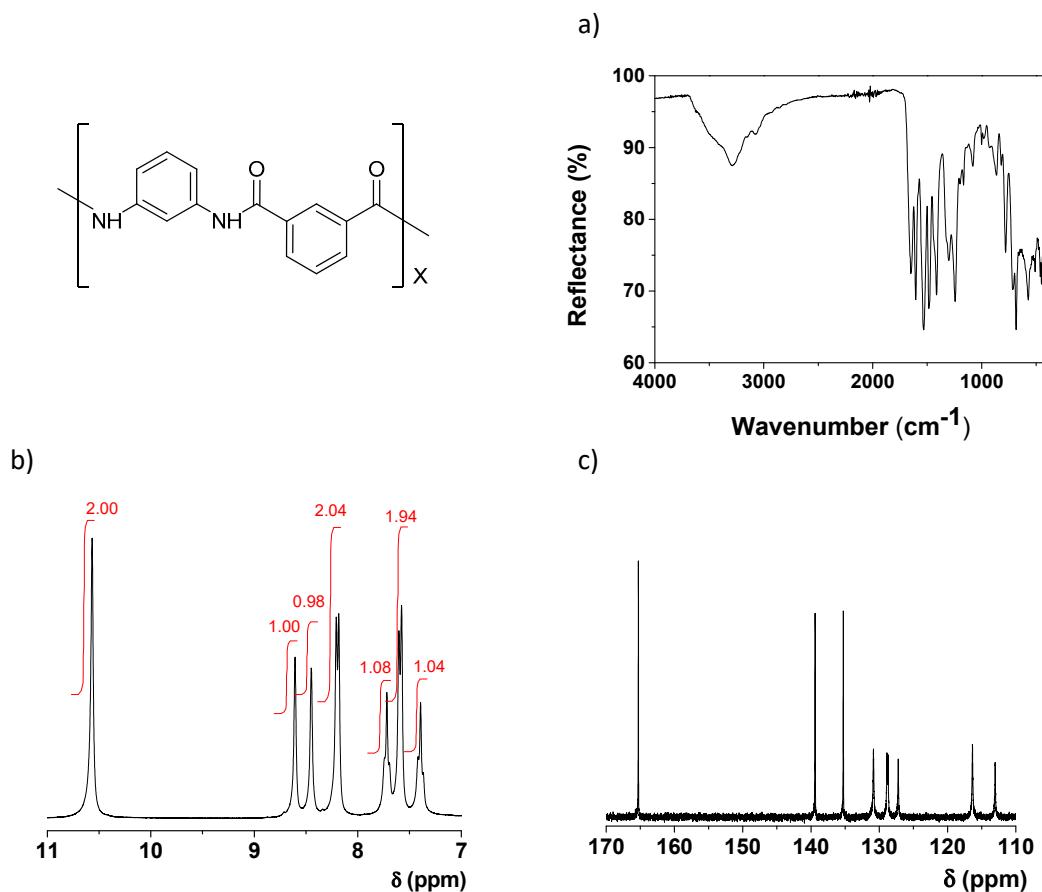
**Figure S8.** Characterization of **CP1** by (a) FTIR, (b)  $^1\text{H}$  NMR, and (c)  $^{13}\text{C}$  NMR.

**Characterization of copolyamide CP2:**



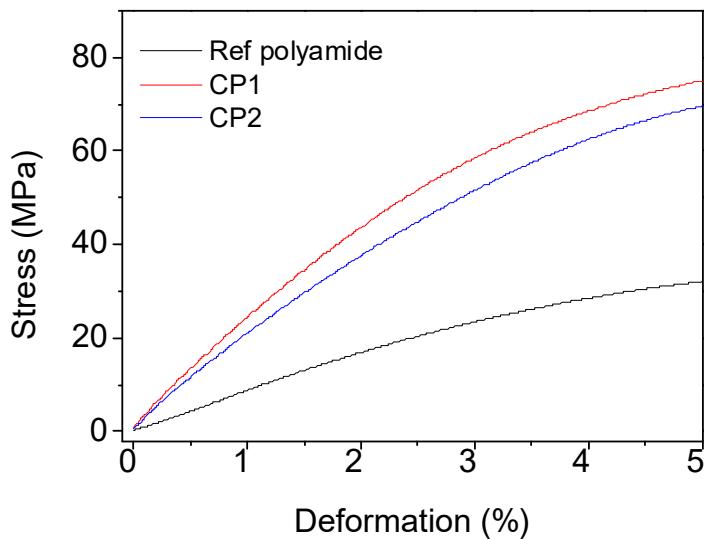
**Figure S9.** Characterization of **CP2** by (a) FTIR, (b)  $^1\text{H}$  NMR, and (c)  $^{13}\text{C}$  NMR.

**Characterization of reference polyamide poly(*m*-phenylene isophthalamide):**



**Figure S10.** Characterization of reference polyamide poly(*m*-phenylene isophthalamide) by (a) FTIR, (b) <sup>1</sup>H NMR, and (c) <sup>13</sup>C NMR.

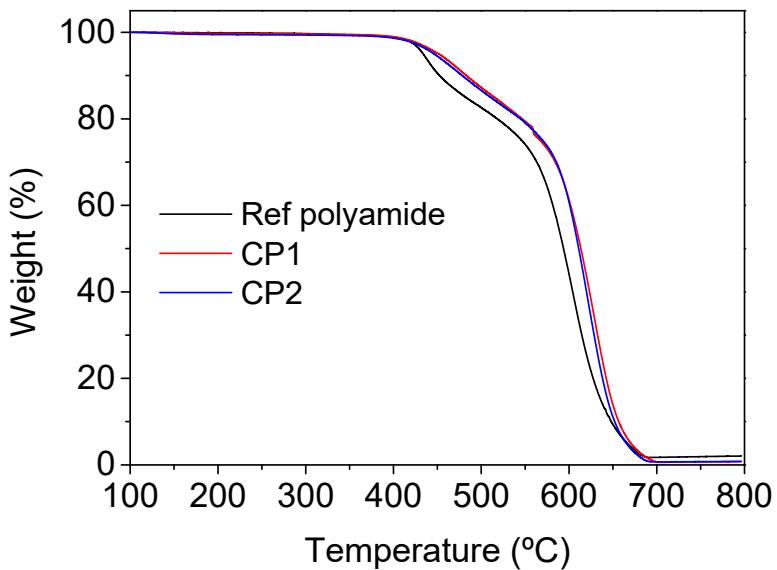
## S6. Mechanical properties of polyamide films



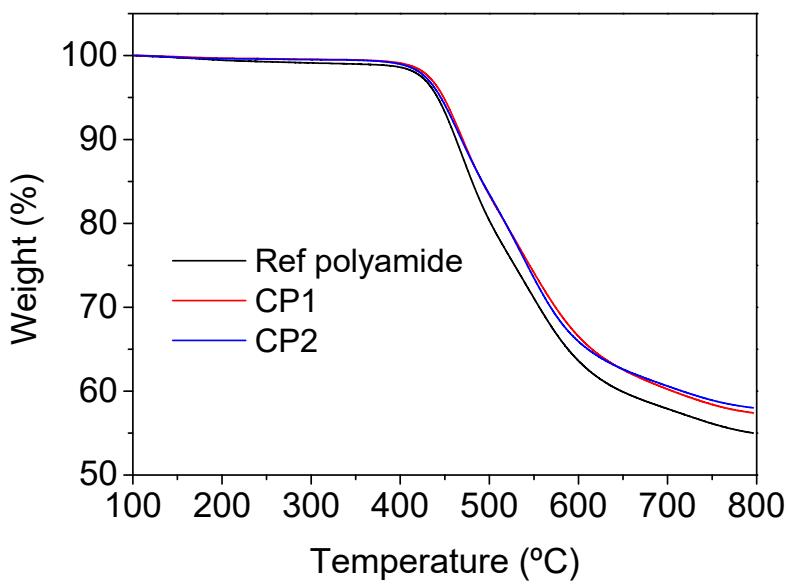
**Figure S11.** Representative stress-strain patterns of copolyamides **CP1**, **CP2**, and reference polyamide poly(*m*-phenylene isophthalamide). The graph has been enlarged at the initial deformation values to show the differences in the Young's Modulus.

## S7. Thermogravimetric analysis of polyamides

a)



b)



**Figure S12.** Thermogravimetric analysis of copolyamides **CP1**, **CP2**, and reference polyamide poly(*m*-phenylene isophthalamide) under a) synthetic air atmosphere, and b) nitrogen atmosphere.