**[Electronic Supplementary Information]**

# Bio-based poly(pentamethylene sebacamide) by solid-state polymerization from bio-based monomers

**Myung Ock Lee,[a,b] Ji Hyun Kim,[b] JaeYun Park[b] and Sang Youl Kim*[a]**

[a]Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejon 34141, Korea

[b]Lotte Chemical Research Institute, 115 Gajeongbuk-ro, Yuseong-gu, Daejeon 34110, Korea

Correspondence to Sang Youl Kim

e-mail: kimsy@kaist.ac.kr

Fax: +82-42-350-2810

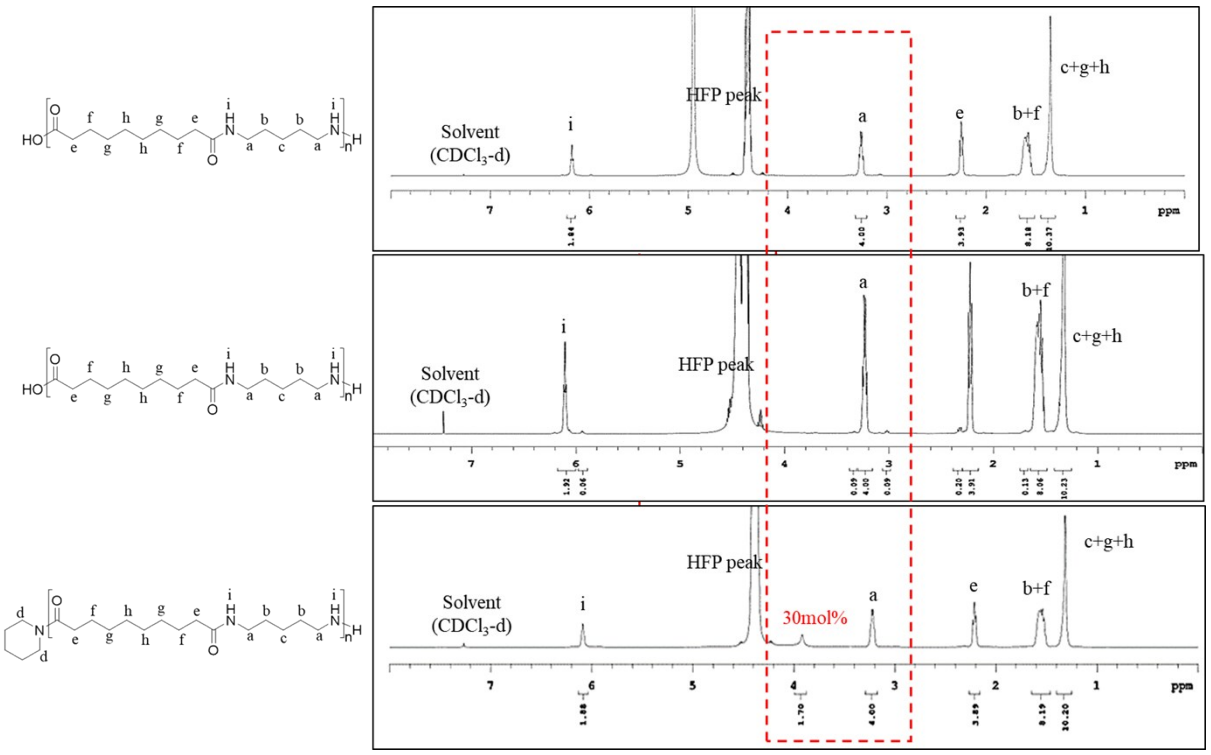


**Figure S1.** $^{1}$H NMR spectra of bio-PA510 a) prepolymer, b) polymer produced by solid-state polymerization, c) polymer obtained by melt polymerization. HFP is 1,1,1,3,3,3-hexafluoro-2-propanol and $CDCl_3$-d is chloroform-d.

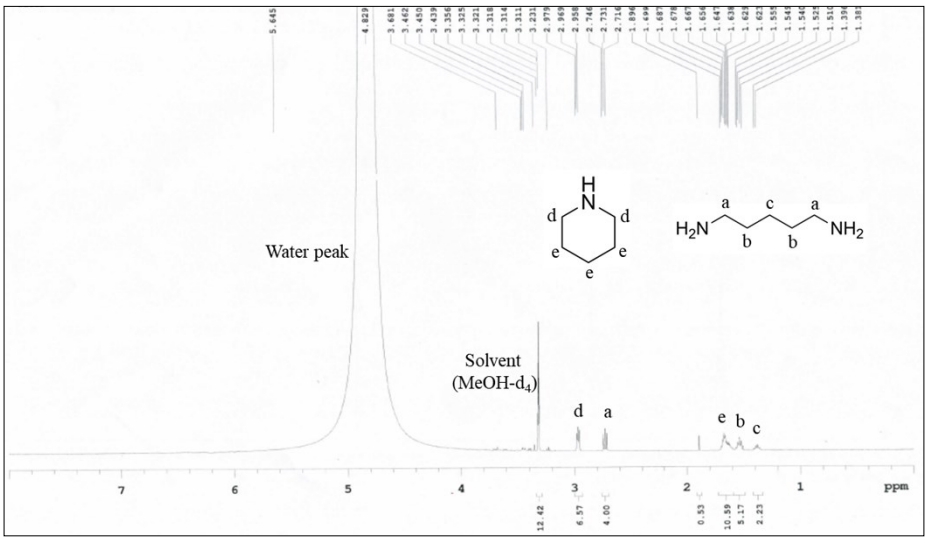


**Figure S2.** $^{1}$H NMR spectrum of the effluent water (Methanol-$d_4$).

It was also observed that not only the cyclic end groups of the oligomer but also the cyclic monomers from cadaverine during the melt polymerization in the effluent water. $^{1}$H NMR analysis of effluent water revealed that the cyclic by-product was piperidine which was formed through elimination of ammonia from cadaverine (Methanol-$d_4$ solvent, Figure S2). The similar results were reported in the case of the polymerization of PA46 from putrescine.[S1, S2]

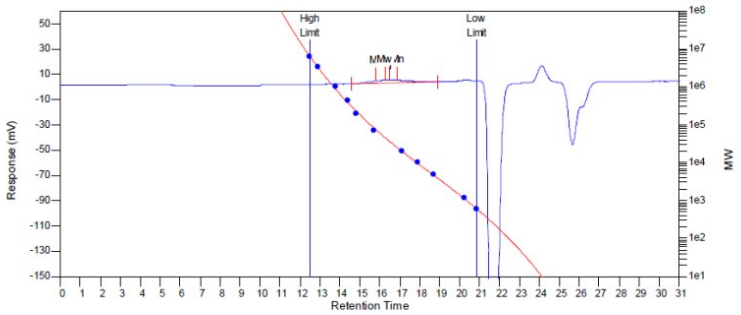


**Figure S3.** GPC chromatogram of bio-PA 510 prepolymer (RV = 1.7, $M_n$ = 25,100 g/mol, $M_w$ = 45,800 g/mol, Đ = 1.82, m-cresol eluent)

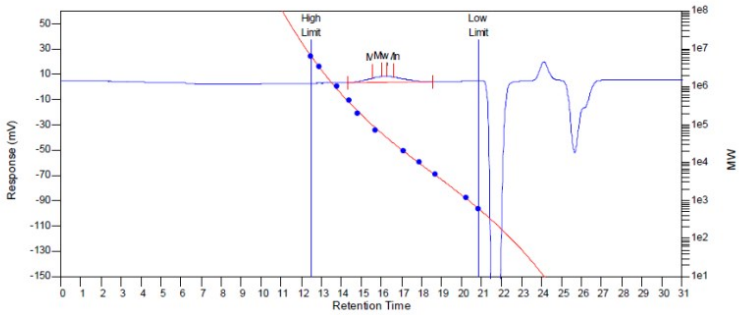


**Figure S4.** GPC chromatogram of bio-PA 510 prepared by SSP (RV = 3.8, $M_n$ = 94,800 g/mol, $M_w$ = 157,000 g/mol, Đ = 1.66, m-cresol eluent)

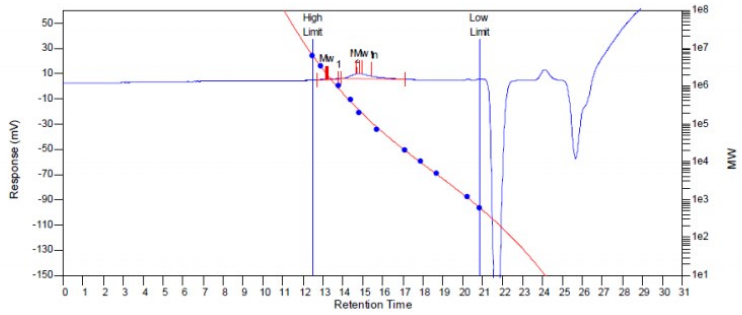


**Figure S5.** GPC chromatogram of bio-PA 510 prepared by melt polymerization (RV = 4.7, $M_n$ = 114,000 g/mol, $M_w$ = 187,000 g/mol, Đ = 1.65, m-cresol eluent)

The molecular weight was analyzed by Gel Permeation Chromatography (GPC, Agilent) with 3 columns (Guard column and two Jordi Resolve 13µm columns) with 1ml/min flow rate at 100°C. m-Cresol was used as solvent with concentration of 1mg/ml. Molecular weight was measured (based on polystyrene standards) with three samples for just checking the molecular weight trend versus the relative viscosity. The results were followings: RV 1.7 (Prepolymer): $M_n$ was 25,100 g/mol and $M_w$ was 45,800 g/mol with 1.82 of Đ value; RV 3.8 of bio-PA510 produced by SSP process: $M_n$ 94,800 g/mol and $M_w$ 157,000 g/mol with 1.66 of Đ value; RV 4.7 of bio-PA510 produced by melt polymerization: $M_n$ 114,000 g/mol and $M_w$ 187,000 g/mol with 1.65 of Đ value.

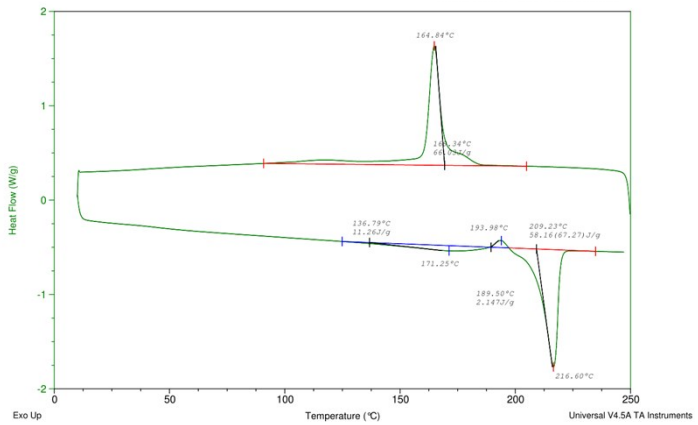


**Figure S6.** DSC curve of bio-PA 510 prepared by SSP.

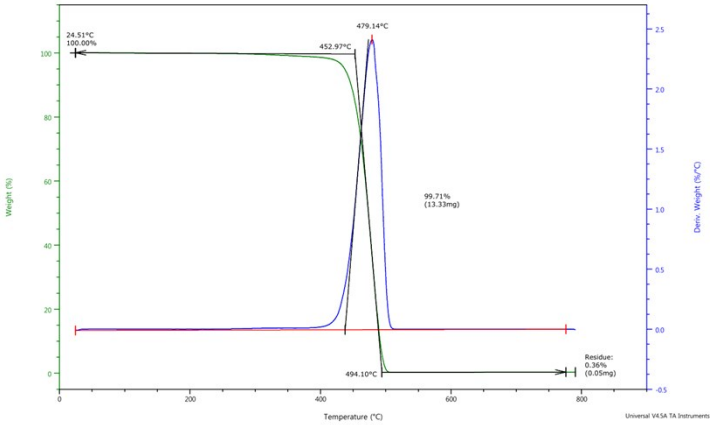


**Figure S7.** TGA curve of bio-PA 510 prepared by SSP.

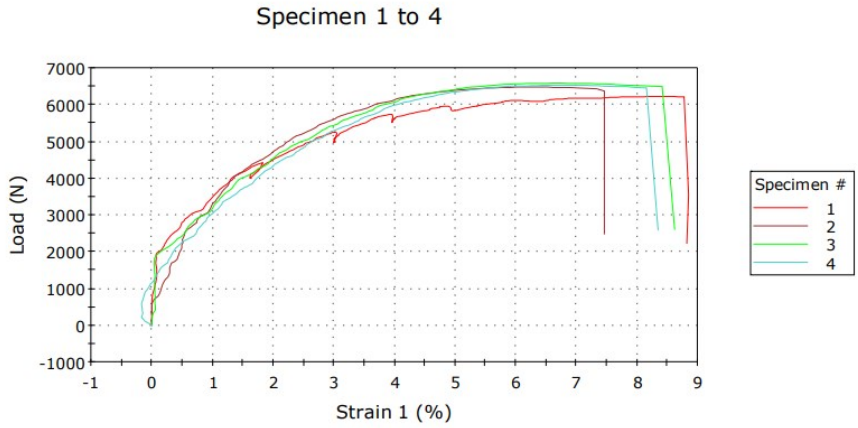


**Figure S8.** Stress-strain diagram of bio-PA 510 prepared by SSP.

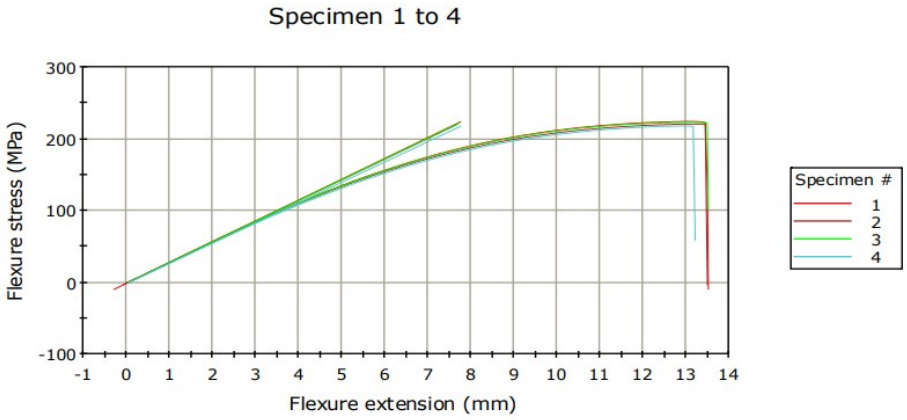


**Figure S9.** Flexure Stress-Flexure extension diagram of bio-PA 510 prepared by SSP.

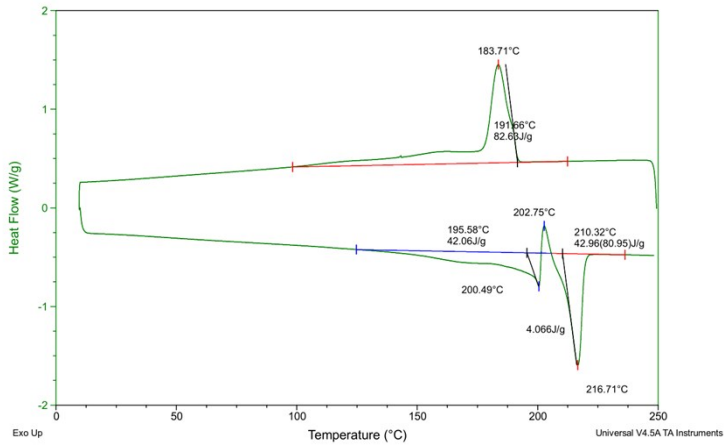


**Figure S10.** DSC curve of PA 612.

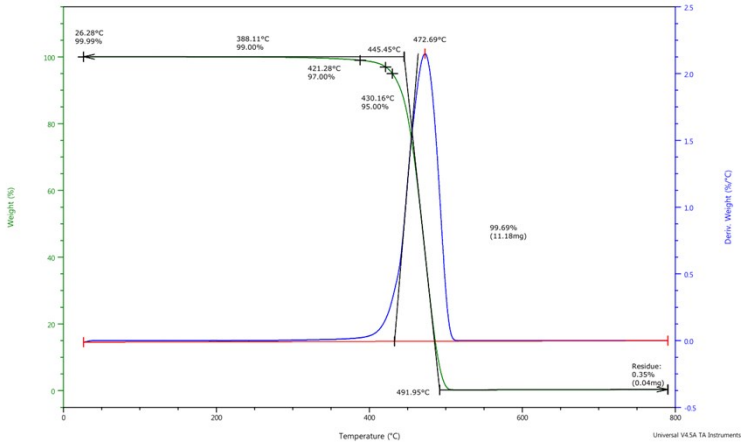


**Figure S11.** TGA curve of PA 612.

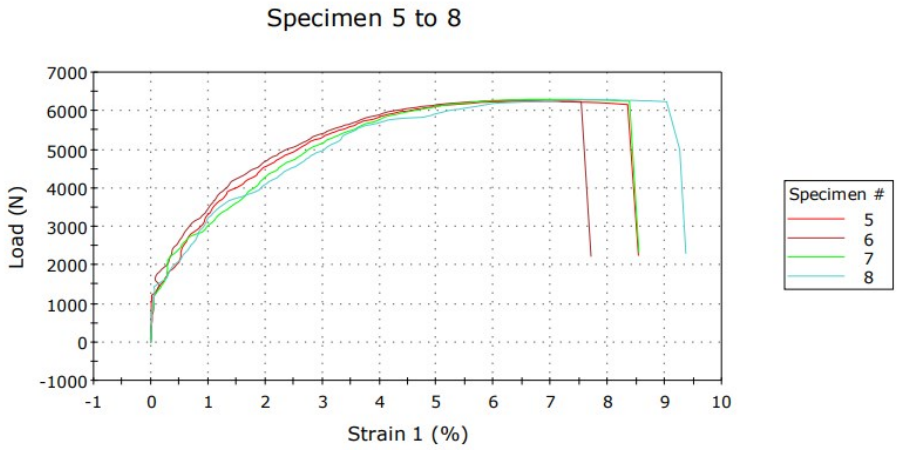


**Figure S12.** Stress-strain diagram of PA 612.

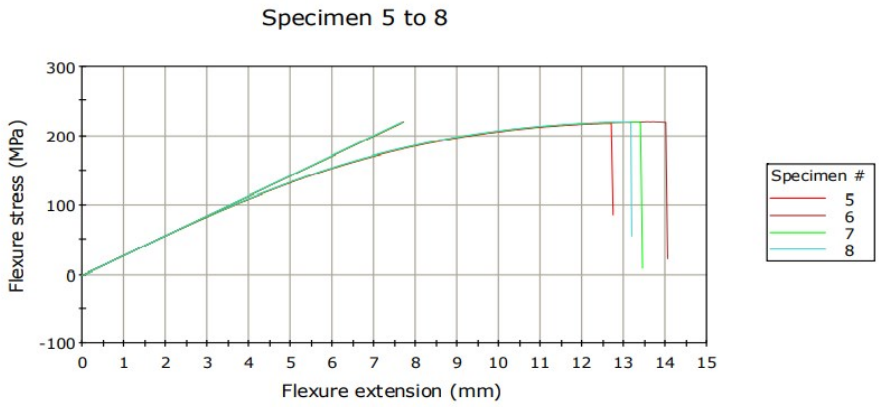


**Figure S13.** Flexure Stress-Flexure extension diagram of PA 612.

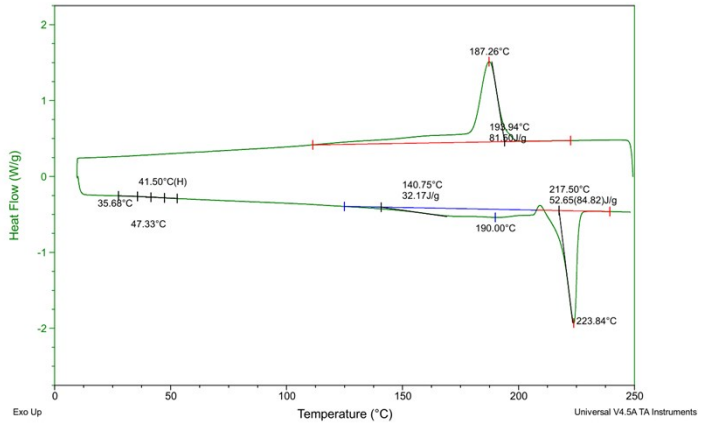


**Figure S14.** DSC curve of PA 610.

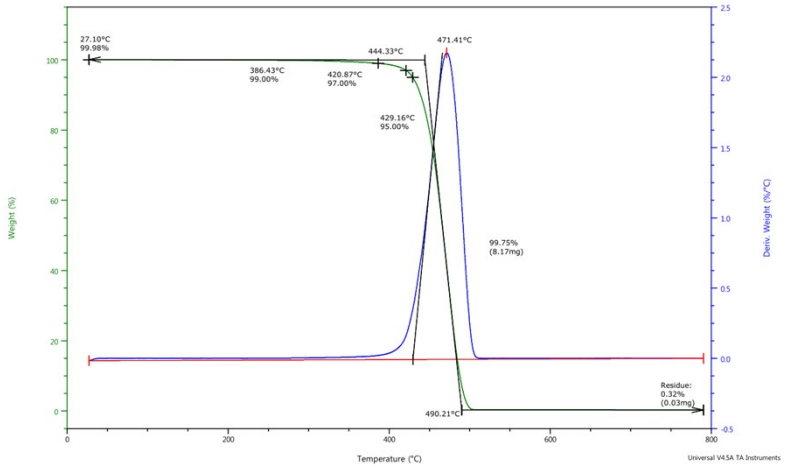


**Figure S15.** TGA curve of PA 610.

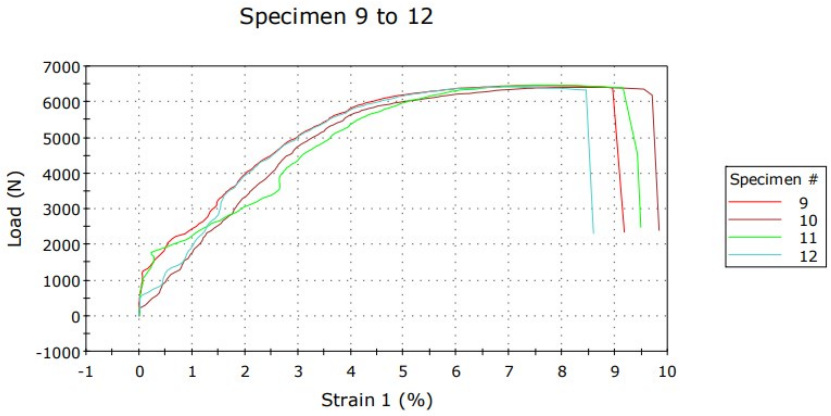


**Figure S16.** Stress-strain diagram of PA 610.

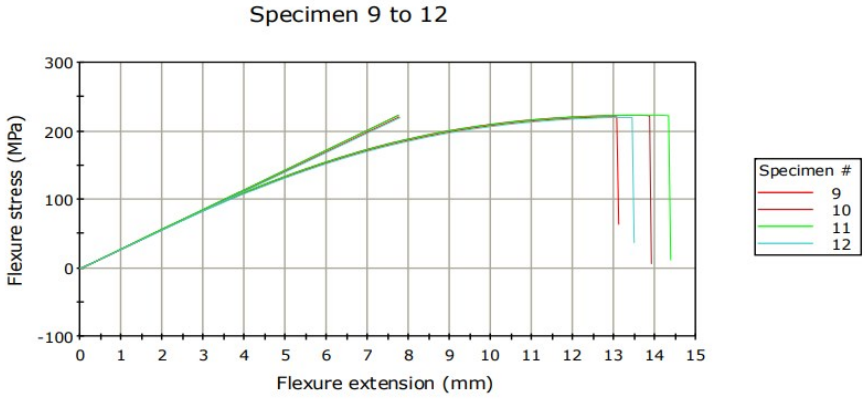


**Figure S17.** Flexure Stress-Flexure extension diagram of PA 610.

**Table S1.** Thermal and mechanical properties of synthesized bio-PA510 and representative commercialized long-chain nylons, PA610 and PA612.

| Properties | Units | PA510 | PA612 | PA610 | Standard |
|---|---|---|---|---|---|
| $T_m$ / $T_d$ (Base resin) | °C | 217/453 | 217/445 | 224/444 | - |
| Glass fiber contents | % | 32 | 31 | 31 | - |
| Density | g/cm$^3$ | 1.3209 | 1.2941 | 1.3163 | ASTM D792 |
| Yield stress (Tensile strength) | MPa | 145 | 141 | 145 | ASTM D638 |
| Breaking stress | MPa | 144 | 141 | 143 | |
| Elongation at break | % | 8 | 8 | 9 | |
| Flexural strength | MPa | 222 | 220 | 222 | ASTM D790 |
| Flexural modulus | MPa | 7270 | 7360 | 7320 | |
| Notched Izod Impact - 23°C, 3T | kg.cm/cm | 13.59 | 19.4 | 19.2 | ASTM D256 |
| Notched Izod Impact - -30°C, 3T | kg.cm/cm | 4.3 | 4.3 | 5.3 | |
| HDT – 18.5kg | °C | 193 | 190 | 194 | ASTM D648 |
| Shrinkage | % | 0.253 | 0.297 | 0.297 | - |

**Table S2.** % Crystallinity of Bio-PA510, PA610, PA612, PA6 and PA66.

| PAs | RV | $\Delta H_f^{obs}$ (J/g) | $\Delta H_f^o$ (J/g) | Crystallinity (%) |
|---|---|---|---|---|
| PA510 | 3.3 | 67.27 | 257 (PA69) | 26 |
| PA610 | 3.0 | 84.82 | 254 | 33 |
| PA612 | 2.8 | 80.95 | 258 | 31 |
| PA6 | 2.5 | 72.16 | 230 | 32 |
| PA66 | 2.5 | 93.78 | 226 | 41 |

$\Delta H_f^{obs}$ : Enthalpy of polymer samples obtained from DSC analysis

$\Delta H_f^0$: Enthalpy of 100% crystalline polymer (theoretical values from References[S3])

$$\text{Crystallinity (\%)} = \frac{\Delta H_f^{obs}}{\Delta H_f^0} \times 100$$

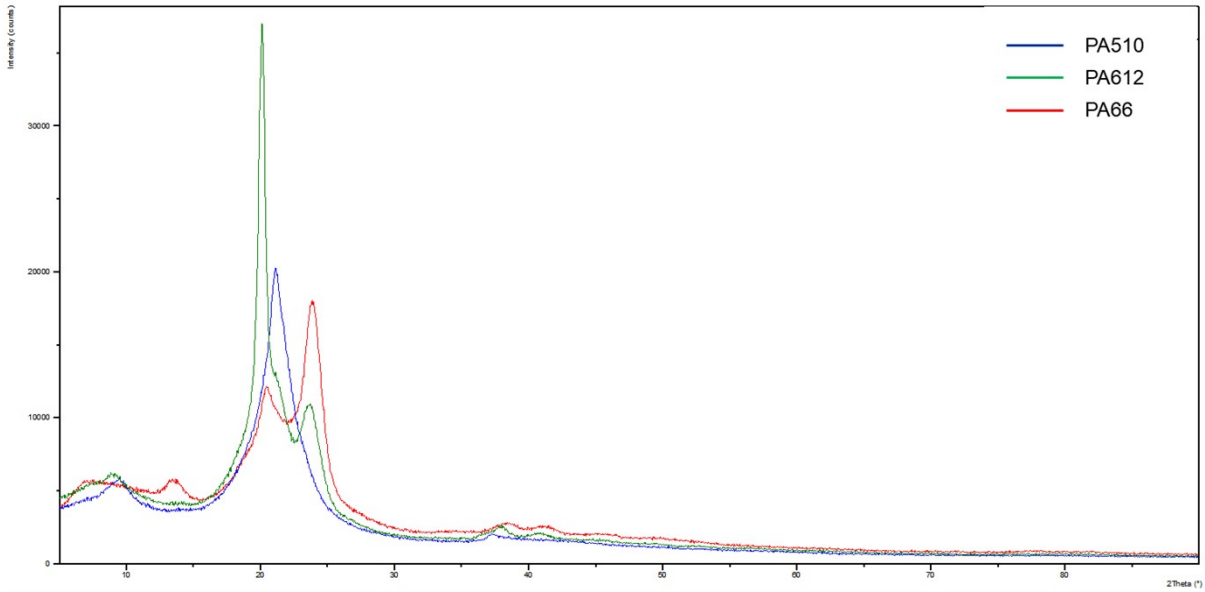


**Figure S18.** XRD patterns of bio-PA510, PA612, and PA66.

## References

S1 R. J. Gaymans, T. E. C. Vanutteren, J. W. A. Vandenberg and J. Schuyer, *J. Polym. Sci.*, 1977, **15**, 537-545.

S2 E. Roerdink and J. M. M. Warnier, *Polymer*, 1985, **26**, 1582-1588.

S3 R. L. Blaine, TA Instruments, Thermal applications note, Polymer heat of fusion.