Supporting Information

Evading the Strength–Ductility Trade-Off Dilemma of Rigid Thermoset by Incorporating Triple Cross-links of Varying Strengths

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1. Main Materials

Diglycidyl ether of bisphenol-A epoxy resin (EPON828, DGEBA) was purchased from TCI Development Co., Ltd., and used as received. Hexamethylenediamine (HDA), 5-amino-1H-benzotriazole (BTraz) and 4-aminopyridine were purchased from J & K Technology Co., Ltd., and used as received. The rest of materials and reagents were obtained from different commercial sources and used without further purification.

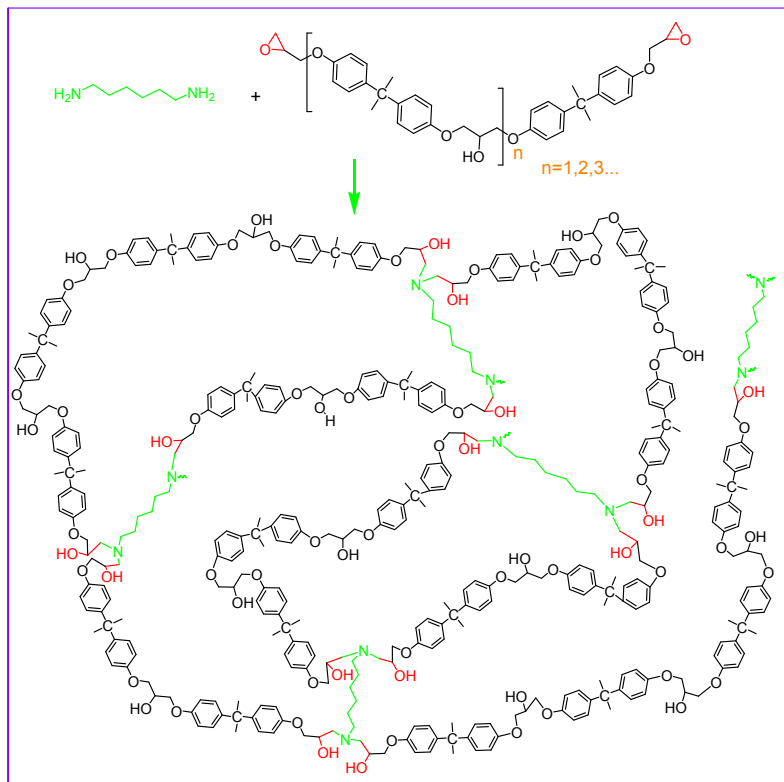## 2. The synthesis route of the hybrid polymer PAHB
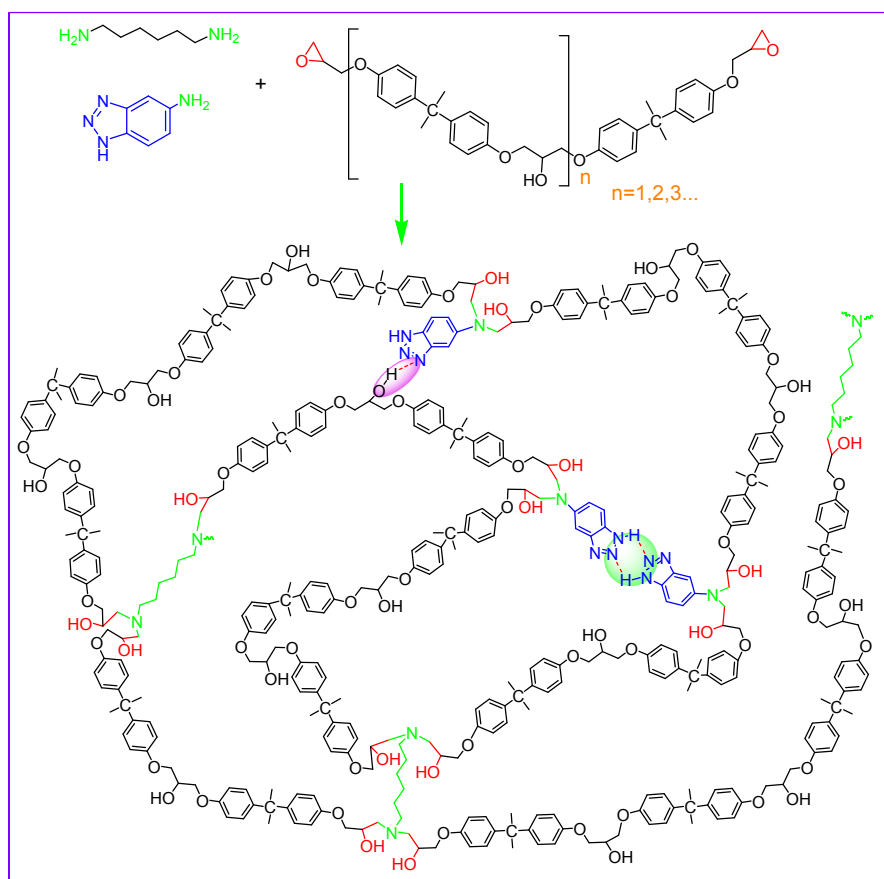
Scheme S1 Synthesis route of the hybrid polymer PAHB.

Table S1 The stoichiometry of the starting materials.

Number	Sample	BTraz	DGEBA	HDA
1	PAHB-0.1	0.1	1	0.45
2	PAHB-0.2	0.2	1	0.4
3	PAHB-0.3	0.3	1	0.35
4	PAHB-0.4	0.4	1	0.3
5	PAHB-0.5	0.5	1	0.25

3. The preparation of chemically cross-linked polymer film PHB

The 0.2 g mixture of DGEBA (EPON828) and HDA ($n_{(DGEBA)}$: $n_{(HDA)}$=2:1) was dissolved in 2.5 mL DMF to form a homogeneous solution, the solution was filtered and subsequently cast onto a clean, flat glass plate, and the cured at 80 °C and 450 torr for 12 hours (Scheme 2).

Scheme S2 Synthesis route of the chemically cross-linked polymer PHB.

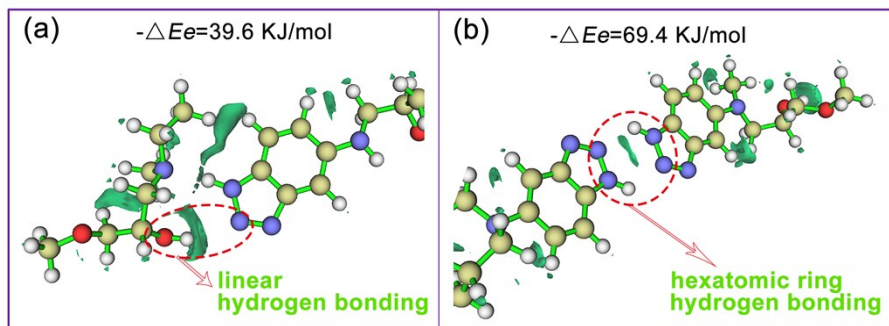## 4. The charge density distribution calculation

Figure S1 NIC plots of gradient isosurfaces (s = 0.5 au) between BTraz group and hydroxy group (a) and between two BTraz groups (b).
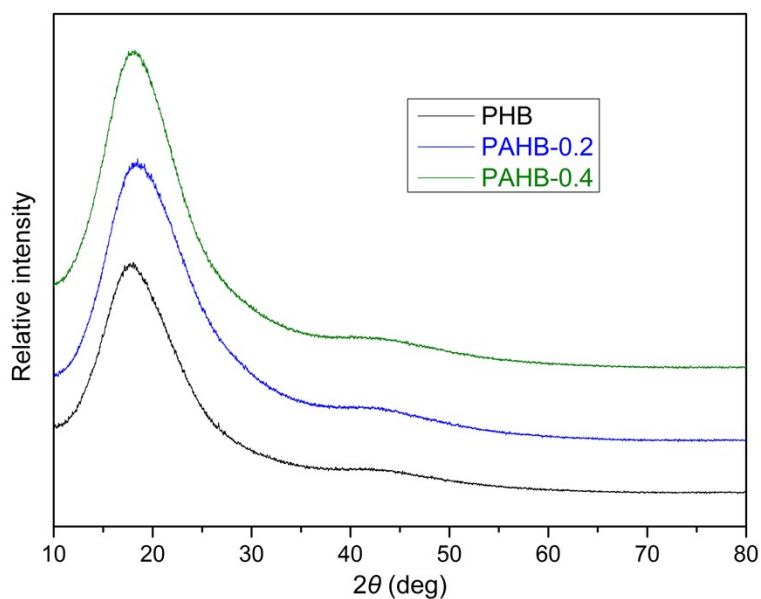
5. The XRD analyses

Figure S2 The WXRD patterns of PHB, PAHB-0.2 and PAHB-0.4 films.

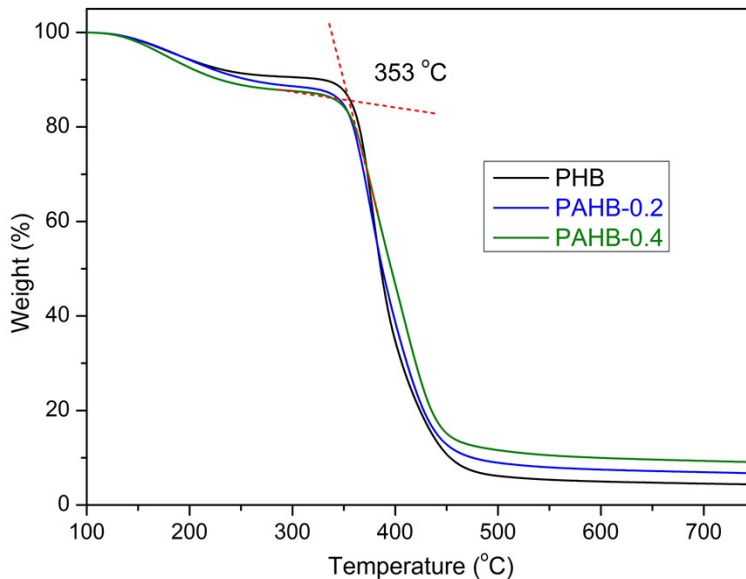## 6. The thermal performances for the polymers PHB, PAHB-0.2 and PAHB-0.4

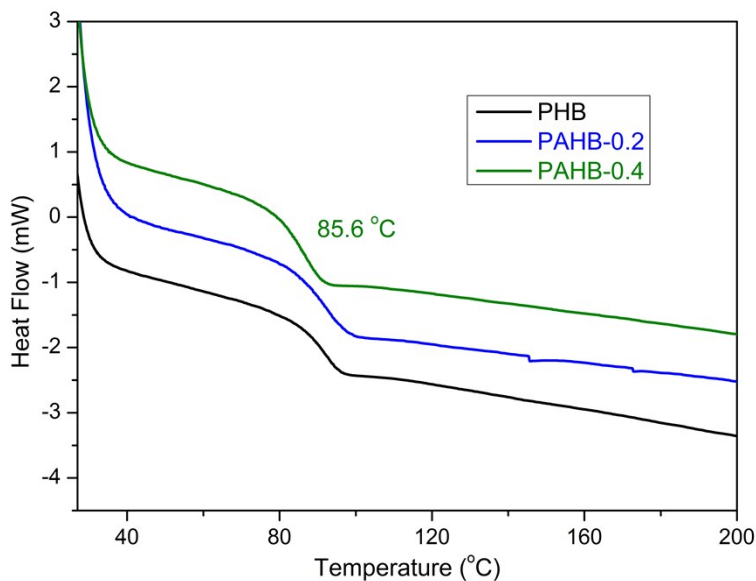**Figure S3** The TGA curves of the polymers PHB, PAHB-0.2 and PAHB-0.4.

Figure S4 The DSC curves of the polymers PHB, PAHB-0.2 and PAHB-0.4.

7. The preparations of hybrid polymer films PYHBs

The 0.2 g mixture of DGEBA, HDA and 4-aminopyridine was dissolved in 2.5 mL DMF to form a homogeneous solution, the solution was filtered and subsequently cast onto a

clean, flat glass plate, and the cured at 80 °C and 450 torr for 12 hours (Scheme 3). By changing the stoichiometry of the starting materials, particularly the mol ratio of 4-aminopyridine and HDA (Table 2), a series of cross-linked amorphous polymer films PYHBs with different content of pyridine (varies from 0.2 to 0.5) were obtained.
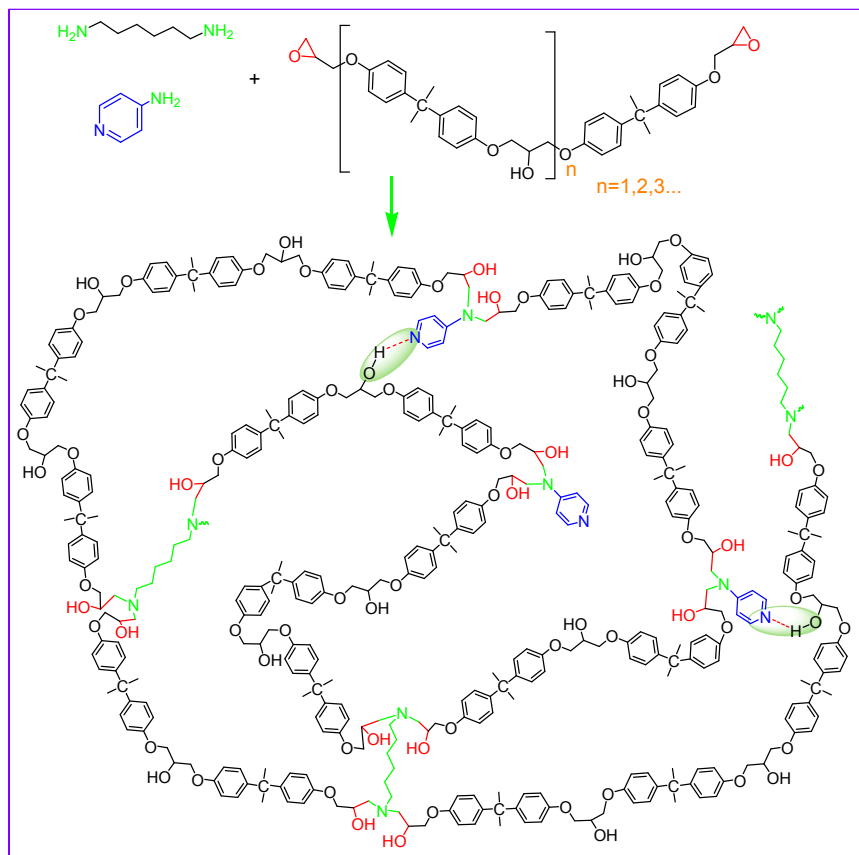
Scheme S3 Synthesis route of the hybrid polymer PYHB.

Table S2 The stoichiometry of the starting materials.

Number	Sample	4-aminopyridine	DGEBA	HDA
1	PYHB-0.2	0.2	1	0.4
2	PYHB-0.3	0.3	1	0.35
3	PYHB-0.4	0.4	1	0.3
4	PYHB-0.5	0.5	1	0.25

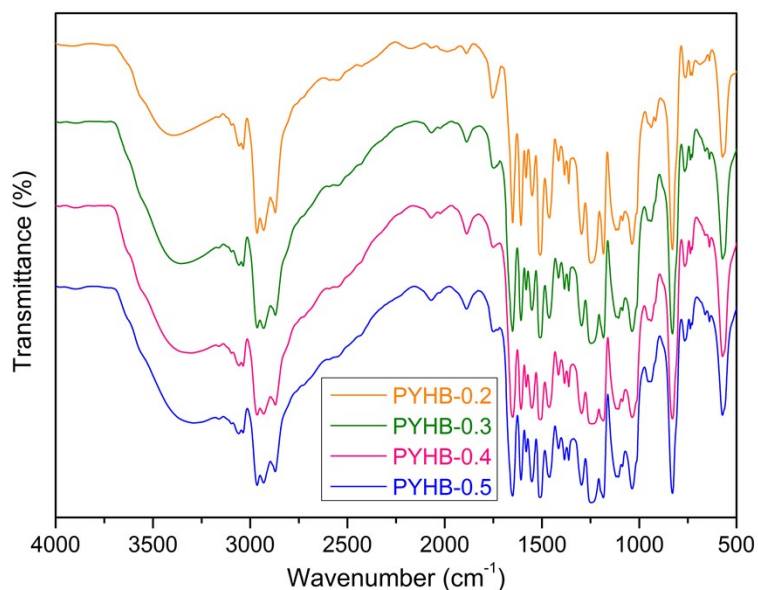## 8. The FT-IR analyses of the PYHBs polymer films

Figure S5 The FT-IR spectra of the PYHBs polymer films.

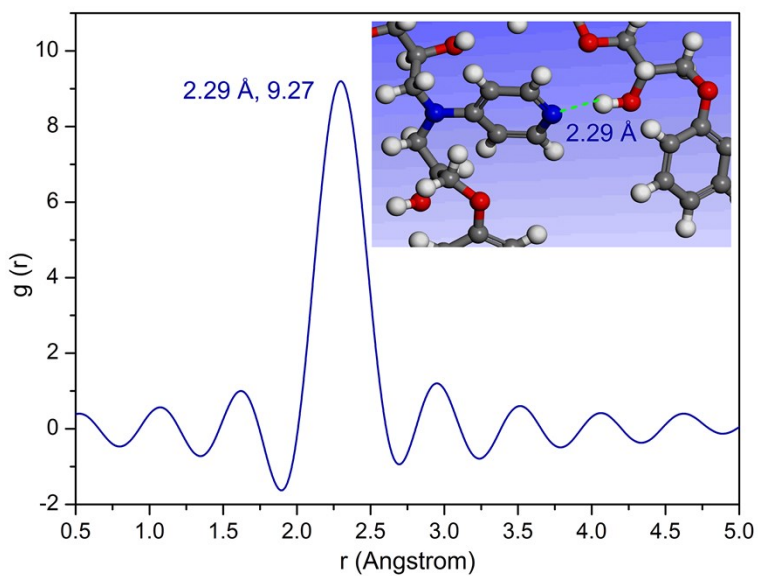## 9. Radial distribution function (RDF) result

Figure S6 Radial distribution function calculation for N atoms of pyridine to the distances of the H atoms of hydroxy groups.

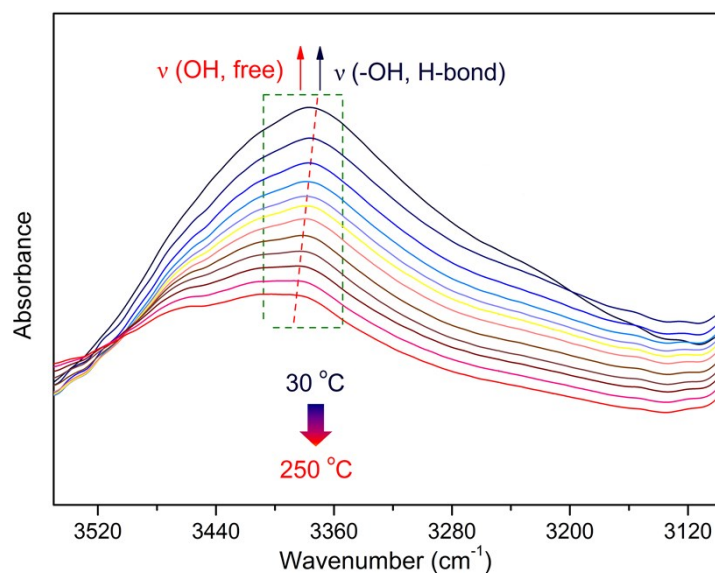## 10. VT-FTIR experiments of the polymer PYHB-0.4

Figure S7 Temperature-dependent FTIR spectra of PYHB-0.4 polymer film upon heating from 30 °C to 250 °C.

11. The average lifetimes of the hydrogen bonds
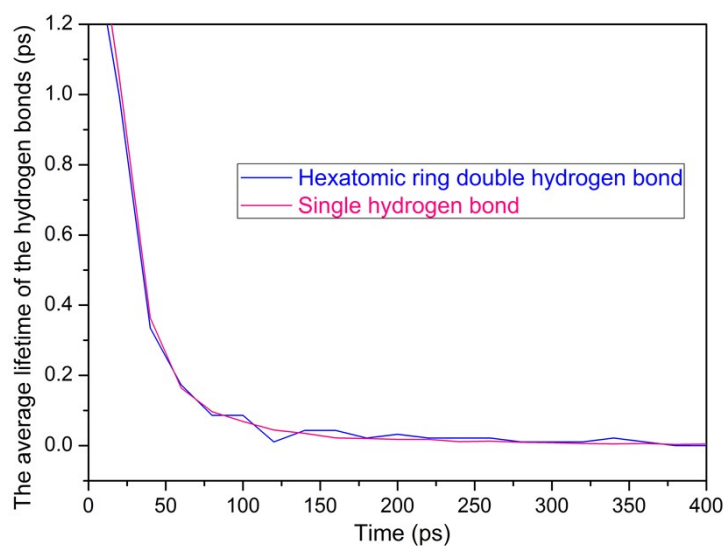
Figure S8 The average lifetimes of the hexatomic ring double hydrogen bonds and the single hydrogen bonds.

12. Cyclic tensile experiments of the polymer films PAHB-0.2 and PAHB-0.4

Figure S9 The cyclic stress-strain curves of PAHB-0.2 film with multiple cycles under the stretching speed $d\varepsilon/dt$= 0.24 mm s^{-1}.

Figure S10 The cyclic stress-strain curves of PAHB-0.4 film with multiple cycles under the stretching speed $d\varepsilon/dt$= 0.24 mm s^{-1}.

13. Density Functional Theory (DFT) Calculation

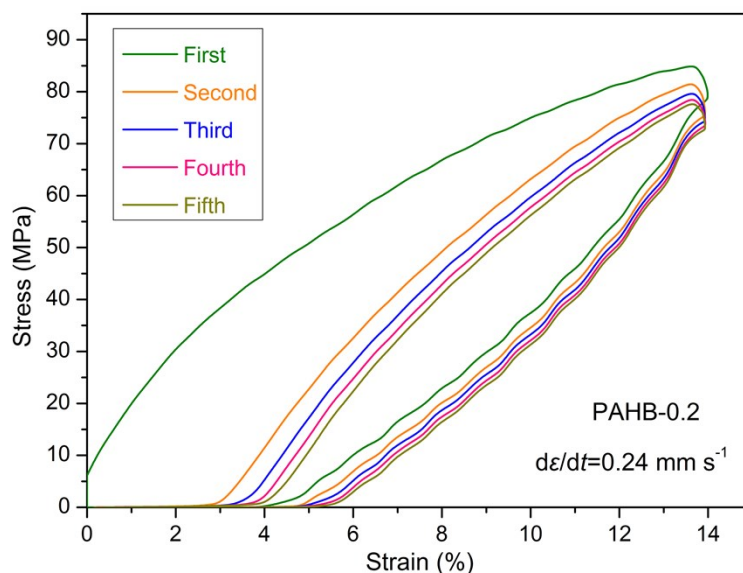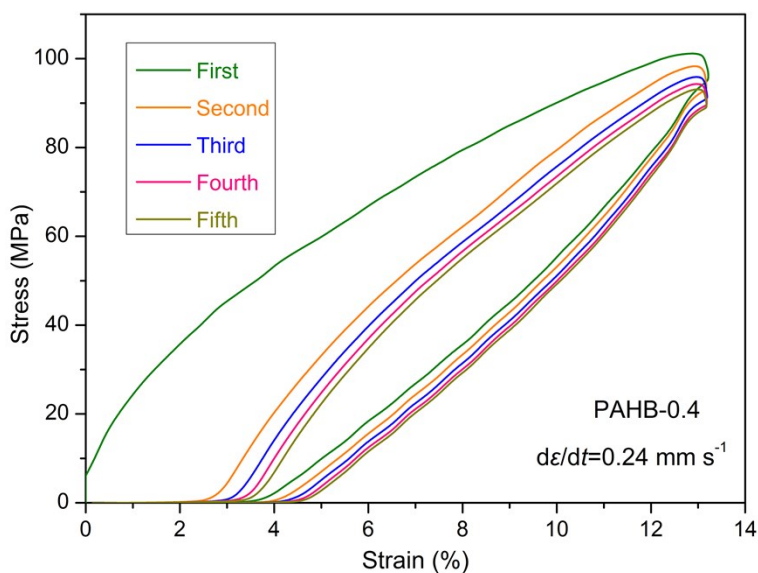The molecules were optimized with density functional theory (DFT) at the BLYPD3/def2-QZVPP method using the Gaussian-09 package and the NIC plots of gradient isosurfaces were analyzed using Multiwfn 3.3.6. Here, the non-covalent interactions (NCI) plots of the cross-linked polymer network unit cell were calculated in real space based on electron density and their reduced gradient using the approach by Yang et al.[1] In this method, analysis of the relationship between quantum-mechanical electron density (ρ) and the reduced density gradient ($s = 1/2(3\pi^2)^{1/3}|\nabla\rho|/\rho^{4/3}$) allows easily detection of the hydrogen bonding interactions.

14. The calculation of radial distribution function

The simulation and calculation were performed using the amorphous cell module of Materials Studio 8.0 with a dreiding force field whose intermolecular parameters were optimized using quantum mechanics. A parent PAHB network was built. The BTraz and hydroxy were randomly distributed in the polymer network. Although size of the parent PAHB network chain is not sufficiently long to represent conformations of a real polymer chain, a previous study has reported a good agreement between experiments and simulations when simulated polycarbonate chains are short (merely 10-15 repeat units on average).[2] Moreover, a periodic boundary condition were imposed and an initial density of 0.6 g cm^{-3} was used to simulate the polymer conformation in bulk under an equilibrium state. The initial structure was optimized by a molecular mechanics technique using the conjugate gradient method. Because this optimized structure might, however, still be in a local energy minimum state, the polymer in simulation box was relaxed through NVT for 1 ns at 800 K with time steps of 0.2 fs. The simulation of high

temperature relaxation was closely followed a protocol suggested previously.[3] After 1 ns of simulated relaxation at 800 K, the system temperature decreased to 273 K. In order to obtain a suitable structure for further analysis, ten different initial structures for each system were built and relaxed according to the procedure mentioned previously. The one with the lowest system energy was selected as the MD result for further radial distribution function analysis.

The radial distribution function, $g_{AB}(r)$, was introduced to describe how density of designated particles varies as a function of distance from a reference particle. Usually, $g_{AB}(r)$ is determined by measuring the ensemble averaged distance between all particle pairs, as follows, $g_{AB}(r)=<n_{AB}(r)>/4\pi r^2 \Delta \rho_{AB}$, where, $n_{AB}(r)$ is the distance of each pair between A (hydrogen atom) and B (nitrogen atom) in the simulation box. <...> represents an ensemble average. $\Delta \rho_{AB}$ is the rate of change in the average number density of hydrogen atom over distance from nitrogen atom.

References

[1] E. R. Johnson, S. Keinan, P. Mori-Sanchez, J. Contreras-Garcia, A. J. Cohen, W. Yang, *J. Am. Chem. Soc.* **2010**, *132*, 6498.
[2] C. F. Fan, T. Cagin, Z. M. Chen, K. A. Smith, *Macromolecules* **1994**, *27*, 2383.
[3] K. J. Lee, W. L. Mattice, R. G. Snyder, *J. Chem. Phys.* **1992**, *96*, 9138.