Supplementary Materials

Effective Reduction of Volumetric Thermal Expansion of Aromatic Polyimide Films by Incorporating Inter-chain Crosslinking

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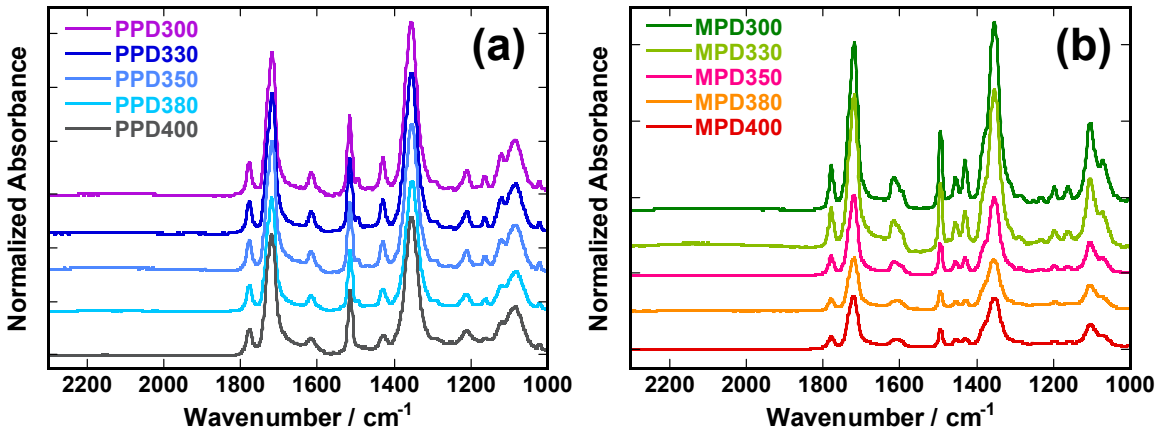
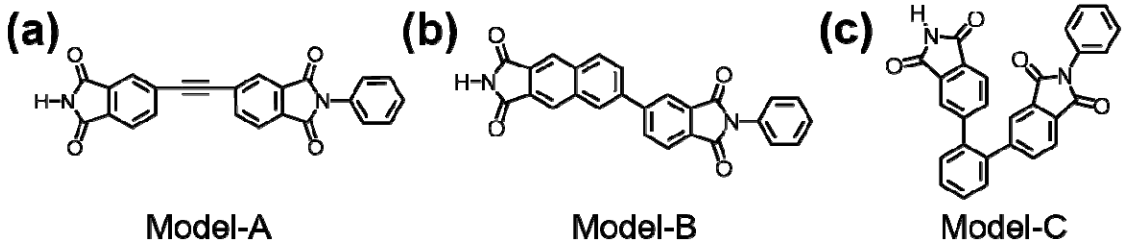


Figure S1. Mid-IR-ATR spectra of (**a**) PPD-PI and (**b**) MPD-PI films cured at different temperatures.



Scheme S1. Structures of model compounds used for the DFT calculation to estimate the packing coefficients before and after crosslink reactions. (**a**) Model-A (before crosslinking) and (**b, c**) Model-B and -C (after crosslink reactions which formed a fused naphthalene or a biphenyl structures).

· **Calculation of intrinsic birefringence (Δn^0) using anisotropic molecular polarizability ($\alpha_{//}$ and $\alpha_{\perp}$)**

Table S1 shows the molecular polarizabilities (α_{11}, α_{22}, α_{33}), intrinsic refractive indices parallel and perpendicular to the molecule long axis ($n^0_{//}$, $n^0_{\perp}$), the intrinsic birefringence (Δn^0) and van der Waals volume (V_{vdw}) of Model-A, -B, and -C. The values of α_{11}, α_{22}, α_{33} were obtained from the DFT calculations, and those of $n^0_{//}$, $n^0_{\perp}$ were obtained based on the following equations by using experimental average refractive index (n_{av}), in which the n_{av}s of Model-A, -B, and -C were assumed as same as that of PPD-300.

$$n^0_{//} = \left[\frac{\alpha_{//}}{\alpha_{\mathrm{av}}}({n_{\mathrm{av}}}^2 - 1) + 1\right]^{\frac{1}{2}} \quad \text{(S1)}$$

$$n^0_{\perp} = \left[\frac{\alpha_{\perp}}{\alpha_{\mathrm{av}}}({n_{\mathrm{av}}}^2 - 1) + 1\right]^{\frac{1}{2}} \quad \text{(S2)}$$

$$\alpha_{//} = \alpha_{11},\ \alpha_{\perp} = \frac{\alpha_{22}+\alpha_{33}}{2},\ \alpha_{\mathrm{av}} = \frac{\alpha_{11}+\alpha_{22}+\alpha_{33}}{3} \quad \text{(S3)}$$

The $\Delta n°$ is given by

$$\Delta n° = n^0_{//} - n^0_{\perp} \quad \text{(S4)}$$

Table S1. Calculated values of average molecular polarizability (α_{av}), principal values of polarizability tensor (α_{11}, α_{22}, α_{33}), van der Waals volume (V_{vdw}), α_{av}/V_{vdw} values, intrinsic refractive indices parallel and perpendicular to the molecule long axis ($n^0_{//}$, $n^0_{\perp}$), and intrinsic birefringence (Δn^0) of Model-A, -B, and –C. The calculation procedures were reported elsewhere.[13]

Model	α_{av} (Å^3)	(α_{11}, (Å^3)	α_{22}, (Å^3)	α_{33}) (Å^3)	V_{vdw} (Å^3)	α_{av}/V_{vdw}	n^0_{av}	$n^0_{//}$	$n^0_{\perp}$	Δn^0
A	52.7	90.0	44.6	23.3	330.1	0.160	1.743	2.118	1.515	0.602
B	54.5	90.2	47.0	26.3	350.6	0.155	1.715	2.052	1.514	0.539
C	53.5	68.2	53.3	39.0	378.8	0.141	1.633	1.767	1.560	0.208

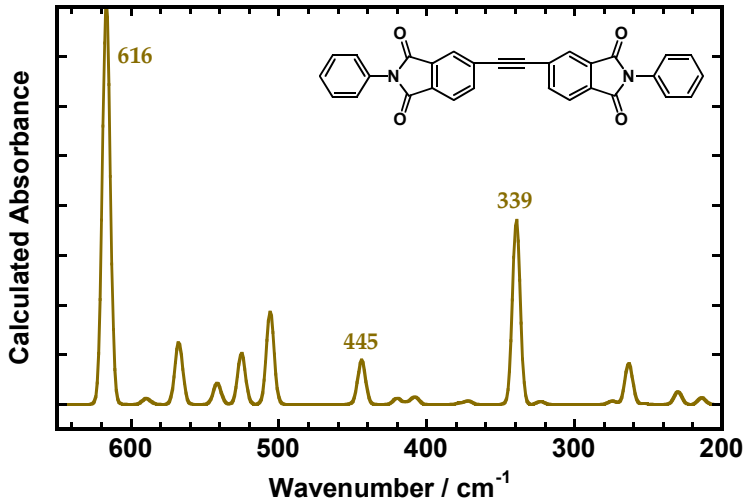


Figure S2. Calculated far-IR absorption spectra of the model depicted in Fig. 3(a).

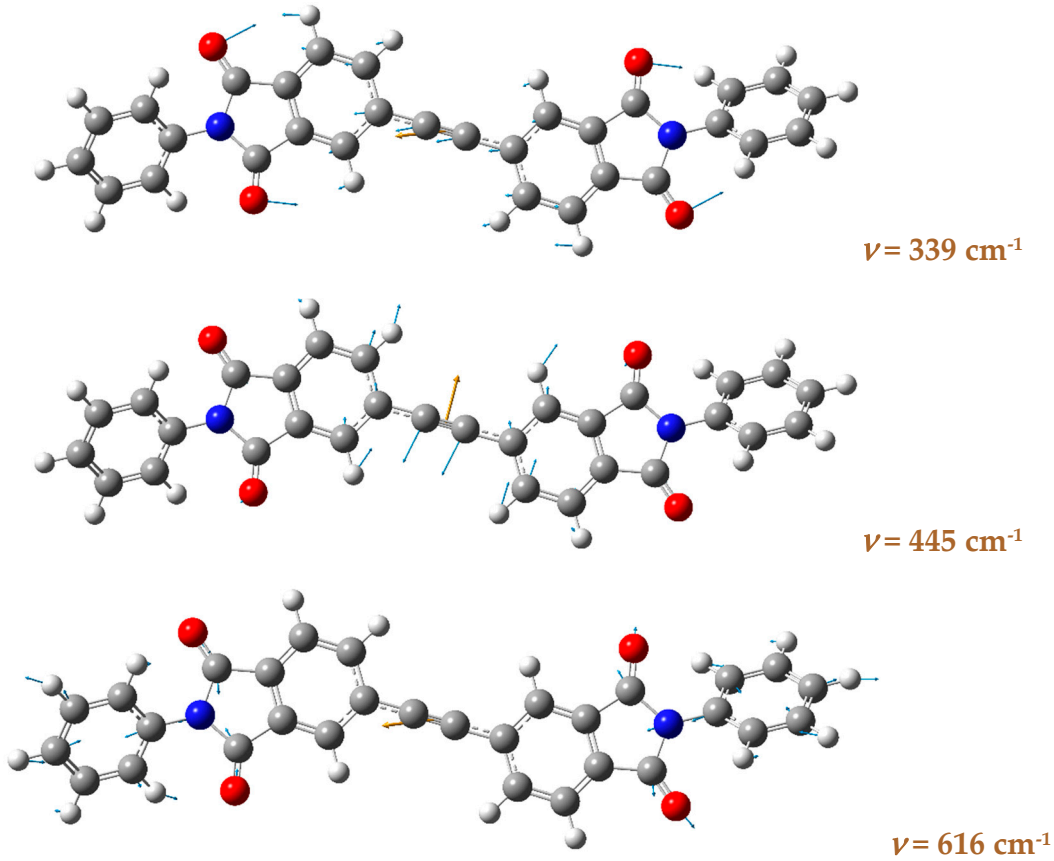


Figure S3. Calculated vibration modes of representative far-IR absorption peaks of the model depicted in Fig. 3(a).

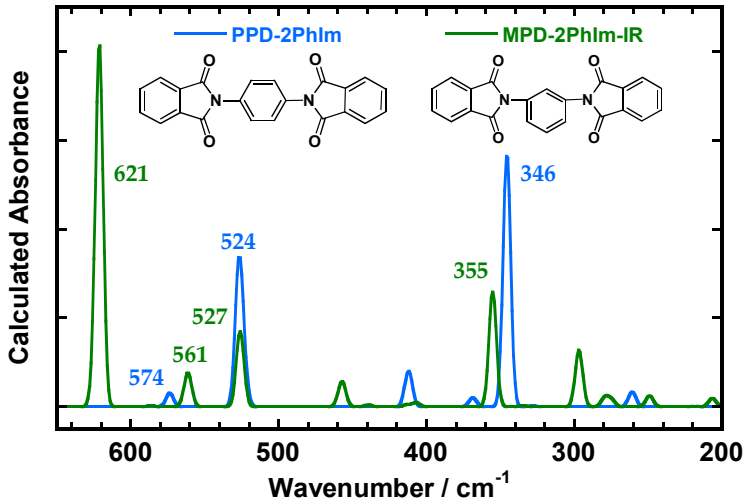


Figure S4. Calculated far-IR absorption spectra of model compounds for PPD-PI and MPD-PI.

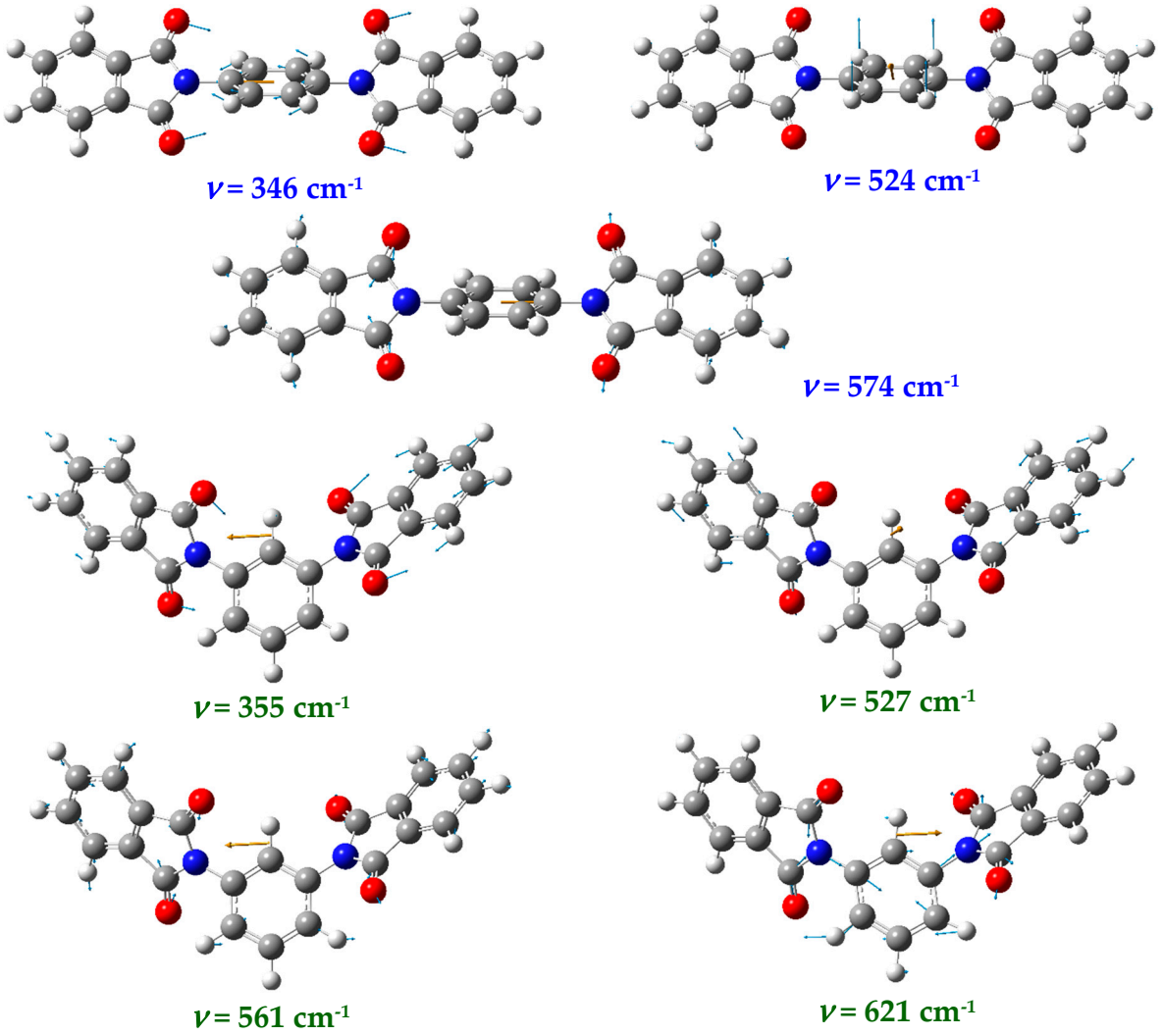


Figure S5. Calculated vibration modes of representative far-IR absorption peaks of the models depicted in Fig. S4.