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# Contribution of blocking positions on the curing behaviors, networks and thermal properties of aromatic diamine-based benzoxazines

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## Highlights

- Aromatic diamine-based benzoxazines with various blocking positions are synthesized.
- Different blocking positions vary the curing temperature of the benzoxazine monomers.
- Hydrogen bonding inhibits autocatalysis in network with arylamine Mannich bridge.
- Changes in blocking positions causes dramatic differences in $T_g$ after polymerization.
- Thermal stability reduces similarly regardless of specific blocking position.

## Abstract

To elucidate the contribution of blocking positions on aromatic diamine-based benzoxazines, we prepared several 4,4’-bis(3,4-dihydro-2*H*-1,3-benzoxazin-3-yl) diphenyl methane monomers with different phenols. The molecular chemical structures of the bi-functional monomers are characterized by FTIR and $^1$H-NMR. Particularly, the newly developed *m*-cresol based benzoxazine is further confirmed by $^{13}$C-NMR and ESI-MS and the oxazine ring position is verified. The curing behaviors are investigated by dynamic differential scanning calorimetry (DSC). Activation energies are analyzed by Kissinger, Ozawa and Starink methods at various heating rates. Due to structure difference in polymerized network, polymer with high amount of arylamine Mannich bridge shows low autocatalysis capability. The glass transition temperature ($T_g$) is closely related to the blocking position while thermal stability decreases comparatively regardless of the blocking position. High arylamine Mannich bridging