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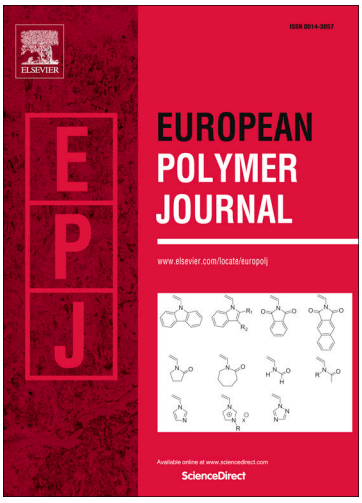

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Pyrogallol-Based Benzoxazines with Latent Catalytic Characteristics: the Temperature-Dependent Effect of Hydrogen Bonds on Ring-Opening Polymerization

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ABSTRACT: Tow kinds of pyrogallol-based di-benzoxazines (PG-FA and PG-A) with a free phenolic hydroxyl between two oxazine rings attaching to the same benzene has been synthesized. The chemical structures of PG-FA and PG-A are identified by ^{1}H NMR, ^{13}C NMR and FTIR tests. The ring-opening polymerization (ROP) behavior of PG-FA and PG-A is monitored by DSC, TGA, FTIR, and in situ FTIR measurements. The pyrogallol-containing benzoxazines show latent active catalysts as it reached at melting condition. The inter- and intramolecular hydrogen bonds from the phenolic hydroxyl and oxygen or nitrogen are converted into weak -OH$\cdots\pi$ intramolecular hydrogen bonding, which easily releases the free phenolic hydroxyl. Afterwards, the free hydroxyl can accelerate the breakage of oxazine ring. Para-position of free phenolic hydroxyl in pygarollol-based benzoxazines is preferentially polymerization by the interaction of imine ions. The temperature-dependent evolution of the chemical structure of PG-FA and PG-A monomers on ROP is consistent with the change of hydrogen bonds.

Keywords: Pyrogallol-Based Benzoxazines; Ring-opening polymerization; Latent active catalysts; Hydrogen bonds; Temperature-dependence

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