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Effect of hydrogen bonds on the polymerization of benzoxazines: influence and control

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This work aims to disclose the reason that prohibited the preparation of highly crosslinked polybenzoxazines. Based on experimental study and computer simulations, we found that the dominant -OH···N hydrogen bond (Type I -OH···N hydrogen bond) of polybenzoxazines blocked high-degree polymerization and resulted in the low crosslink density by decreasing the charge densities of corresponding hydroxyl groups on phenols. As a solution, by introducing additional hydrogen-bonds acceptors, the formation of Type I -OH···N hydrogen bonds could be suppressed, which enable high-degree polymerization of benzoxazines. This novel insight about benzoxazine polymerization is anticipated to help researchers explore more kinds of polybenzoxazines with enhanced properties.

Introduction

Polymers, composed of a large number of small molecules, have been applied in nearly all areas of daily life and major industries due to their excellent properties which are strongly influenced by details of the chain structures, like molecular weight. Hence, how to convert monomers into polymers has attracted wide extensive interest in scientific and industrial community. Nevertheless, lots of puzzles still remain, particularly in thermosets as in the case of phenolic resins. This is because once thermosets formed through chemically linking by covalent bonds during polymerization, these crosslinked networks resist heat softening and solvent attack which make thermosets are hard to be characterized.[1]

Polybenzoxazines, belong to the category of phenolic resins, prepared by thermal polymerization of the corresponding monomer, 3,4-dihydro-2*H*-3-substituted-1,3-benzoxazine (benzoxazine) or its derivatives,[2-4] present a large family of materials which are applied in many fields like microelectronics, aeronautical technology and astronautic industry due to their highly desirable properties, such as good mechanical properties,[5-8] low water absorption,[9] near-zero volumetric shrinkage[10] and no volatile release during polymerization. However, some issues still exist for these materials such as degradation and mechanical properties, generally resulting from the low crosslink density of polymers. To address these issues, many methods have been developed to increase the crosslink density, for instance, by copolymerizing with other resins of high crosslink density[11-14] or incorporating additional polymerizable groups[15-18]. However, it is still a mystery that the reason behind causing the low crosslink density. Previous research speculated that hydrogen bonds may hinder polymerization and produce the low crosslink density.[19-21] Nevertheless, this viewpoint has not been proved yet. Obviously, more investigation on this problem is highly desirable and valuable.

Usually, thermosets are obtained for polybenzoxazines, which are made from monomers consisting of multiple oxazine ring groups. During polymerization, covalent crosslinking happened and resulted in crosslinked networks which resist heat softening and solvent attack, making polybenzoxazines hard to be characterized.[1] To investigate the detailed mechanism influencing the polymerization, soluble products are required to build the relationship between reaction conditions and polymerization results. Hence, in this work, three monomers consisting of single oxazine ring group which can form dissolvable polybenzoxazines are applied to explore the polymerization. The results showed that -OH···N hydrogen bonds of polybenzoxazines (Type I -OH···N hydrogen bond) blocked high-degree polymerization through decreasing the charge densities of corresponding hydroxyl groups on phenols (Scheme 1, Path a). As one of the solutions, additional hydrogen-bonds acceptors were introduced to control the formation of Type I -OH···N hydrogen bonds and finally high-degree polymerization was achieved (Scheme 1, Path b). Detailed analysis and discussions are provided below.

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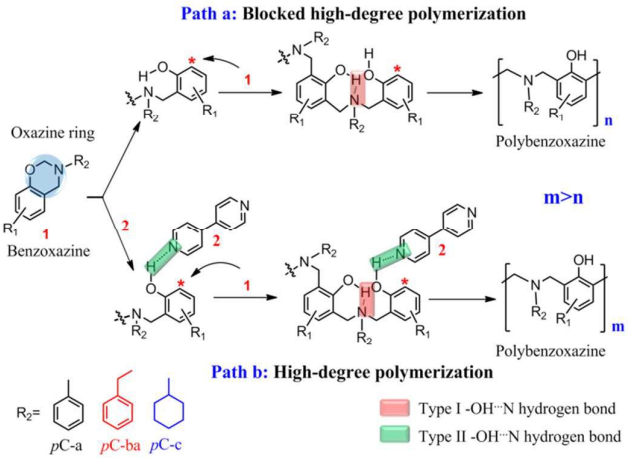


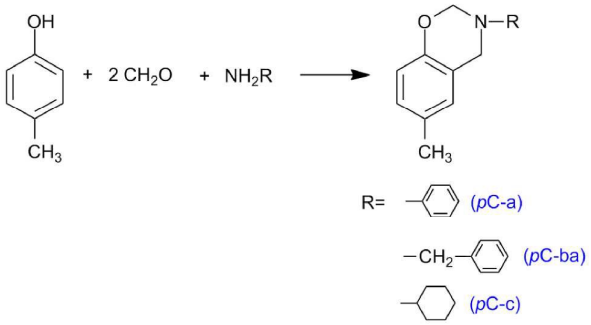
Scheme 1 Polymerization of benzoxazines

Experimental

All the materials and measurements used in this study are described in the ESI.

Synthesis of *p*-cresol-monoamines based on benzoxazines

Three *p*-cresol-monoamines based benzoxazines were synthesized as Scheme 2 shown.



Scheme 2 Synthesis of *p*-cresol-monoamines based benzoxazines

Sythesis of 3,4-Dihydro-6-methyl-3-phenyl-2*H*-1,3-benzoxazine (*p*C-a)

Aniline (46.5 g, 0.5 mol), *p*-cresol (54 g, 0.5 mol), paraformaldehyde (33 g, 1.1 mol) and toluene (48.8 mL) were added into a 250 mL three-necked bottle and stirred at 80 °C for 5h. Then, the solution was cooled to room temperature. After that, this solution was washed by 4 wt% NaOH solution and deionized water. After recrystallization in acetone/ethanol (5/15 mL) and drying in a vacuum oven, 100.7 g (89.5% yields) of white solid (*p*C-a) with a melting peak of 48.8 °C and a polymerization peak temperature of 265.4 °C were obtained.

^{1}H NMR (DMSO-d6, ppm, δ): 2.18 (s, 3H, -C**H**$_3$), 4.60 (s, 2H, Ar-C**H**$_2$-N-), 5.39 (s, 2H, -N-C**H**$_2$-O-), 6.59-7.24 (s, 8H, Aromatic *H*).

FTIR (cm^{-1}): 947 (oxazine ring), 1037 and 1227 (Ar-O-CH$_2$-).

Sythesis of 3,4-Dihydro-6-methyl-3-benzyl-2*H*-1,3-benzoxazine (*p*C-ba)

*p*C-ba was synthesized from *p*-cresol, benzylamine and paraformaldehyde. Synthesis procedures were carried out in analogy to the synthesis of *p*C-a. 94.3 g (78.9% yields) of white solid (*p*C-ba) with a melting peak of 69.5 °C and a polymerization peak temperature of 254.8 °C were obtained.

^{1}H NMR (DMSO-d6, ppm, δ): 2.18 (s, 3H, -C**H**$_3$), 3.33 (s, 2H, -N-C**H**$_2$-Ar), 3.66(s, 2H, Ar-C**H**$_2$-N-), 4.80 (s, 2H, -N-C**H**$_2$-O-), 6.67-7.00 (s, 3H, Aromatic *H*).

FTIR (cm^{-1}): 938 (oxazine ring), 1076 and 1220 (Ar-O-CH$_2$-).

Sythesis of 3,4-Dihydro-6-methyl-3-cyclohexyl-2*H*-1,3-benzoxazine (*p*C-c)

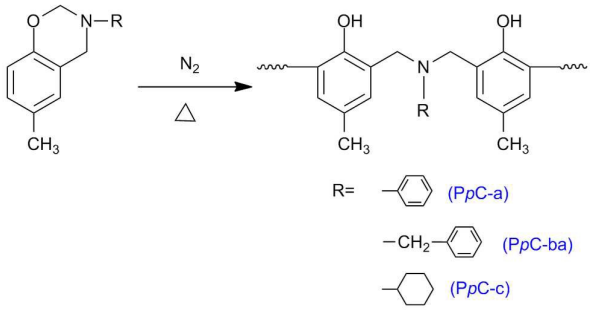
*p*C-c was synthesized from *p*-cresol, cyclohexylamine and paraformaldehyde. Synthesis procedures were carried out in analogy to the synthesis of *p*C-a. 49.3 g (42.9% yields) of white solid (*p*C-c) with a polymerization peak temperature of 261.3 °C was obtained.

^{1}H NMR (DMSO-d6, ppm, δ): 2.51 (s, 3**H**, -CH$_3$), 4.96 (s, 2H, Ar-C**H**$_2$-N-), 4.71 (s, 2H, -N-C**H**$_2$-O-), 6.43-7.00 (s, 3H, Aromatic *H*).

FTIR (cm^{-1}): 934 (oxazine ring), 1039 and 1225 (Ar-O-CH$_2$-).

Preparation of polybenzoxazines from *p*C-a, *p*C-ba and *p*C-c

As Scheme 3 shown, polybenzoxazines with different conversions were prepared in three-necked bottles by polymerizing *p*C-a, *p*C-ba and *p*C-c at 160 °C for different time (1, 2, 4, 8, 12, 24h) under nitrogen atmosphere, respectively. And the corresponding polybenzoxazines were successively denoted as P*p*C-a, P*p*C-ba and P*p*C-c.

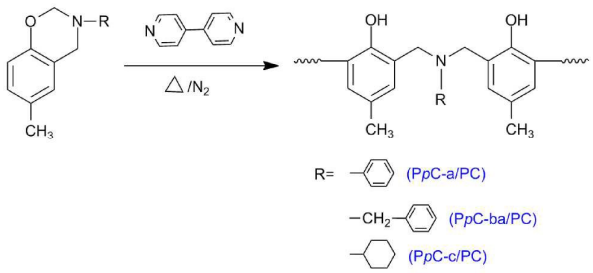


Scheme 3 Preparation of P*p*C-a, P*p*C-ba and P*p*C-c from *p*C-a, *p*C-ba and *p*C-c

Preparation of the blends of *p*-cresol-monoamines based benzoxazines and 4,4'-bipyridine

The molar ratios of *p*-cresol-monoamines based benzoxazines and 4,4'-bipyridine in the blends were 2/1, 2/1 and 2/1, respectively. The procedure was as follows. *p*C-a or *p*C-ba or *p*C-c and 4,4'-

bipyridine were introduced into a 250 mL flask equipped with a beater in the ratios stated above. After polymerized at 160 °C for different time (0.5, 1, 1.5, 2, 3, 4, 8, 12, 24h) under nitrogen atmosphere, the corresponding crude polymers were denoted as P*p*C-a/PC, P*p*C-ba/PC and P*p*C-c/PC (depending on the benzoxazines), respectively. After dissolving P*p*C-a/PC, P*p*C-ba/PC and P*p*C-c/PC in tetrahydrofuran and precipitating in methanol, and removing solvents using a rotary evaporator, yellow solids were gained and respectively denoted as P*p*C-a/P, P*p*C-ba/P and P*p*C-c/P.



Scheme 4 Preparation of blends of *p*-cresol-monoamines based benzoxazines and 4,4′-bipyridine

Results and discussion

To probe the degree of polymerization, the conversions (α)/molecular weights ($\overline{M_n}$) relationship was first established for *p*C-a, *p*C-ba and *p*C-c under isothermal condition at 160 °C as shown in Fig. 1. All of the conversions and molecular weights increased as polymerization time increased, but molecular weights increased a little. After polymerizing for 24h, the α of *p*C-a, *p*C-ba and *p*C-c are 96.2%, 90.1% and 93.3%, while $\overline{M_n}$ are 1093, 770 and 725 D, respectively. The results indicated that almost all benzoxazines have been consumed under the present conditions, but only oligomers are gained. In other words, the ring-opening reactions reacted easily, but the consumed benzoxazines did not contribute much to the propagation of polymer chains (that is, high-degree polymerization of benzoxazines are blocked). Considering that polybenzoxazines were liquid under the polymerization conditions, diffusion of reaction intermediates should not be the limiting factor. Thus, the obstacle of high-degree polymerizations should mainly exist in benzoxazines' chain propagation step. The main reaction sites on polybenzoxazines are the *ortho*-position carbon of the generated phenol (the position of asterisk, Scheme 1).[22-25] Hence, the reaction reactivity of the *ortho*-position carbon of phenol was checked firstly, which was strongly related to charge densities of adjacent phenol groups. The calculation results showed that the charged densities of *ortho*-position of phenol didn't change much if only the degree of polymerization ($\overline{X_n}$) increased. For example, the charged densities are -0.057, -0.057 and -0.056 respectively when $\overline{X_n}$ are 3, 4 and 6 in the case of *p*C-a (Fig. S4). However, with hydrogen bonds involved, the charged densities will change significantly.

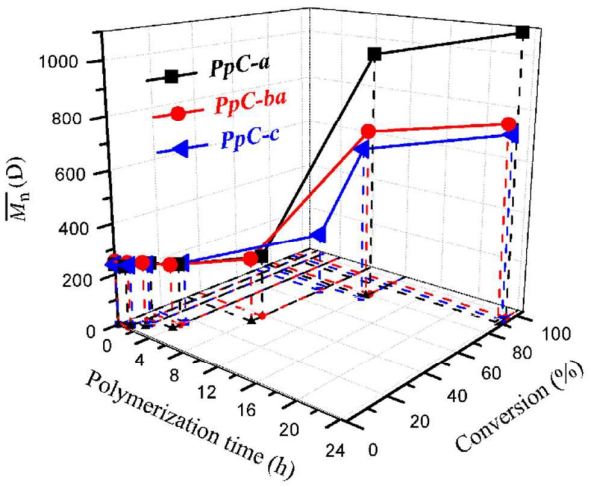


Fig. 1 The conversions (α) and molecular weights ($\overline{M_n}$) of P*p*C-a, P*p*C-ba and P*p*C-c after polymerizing different time at 160 °C.

In the classical bulk polybenzoxazines, hydrogen-bond donor is the generated -OH, and the acceptors are -OH, N-Ar and π respectively, forming -OH···O, -OH···N (-OH···N and -O$^-$···$^+$HN formation, denoted as Type I -OH···N hydrogen bond) and -OH···π hydrogen bonds.[26-31] After studying hydrogen bonds formation using FTIR (Fig. S11), however, we found that the dominant hydrogen bond is Type I -OH···N hydrogen bond , *e.g.*, the fractions of -OH···N hydrogen bonds of P*p*C-a, P*p*C-ba and P*p*C-c are respectively 86.2 %, 86.9 % and 93.0 % after polymerizing for 24h (Fig. 2). To further support this view, this work applied molecular dynamics (MD) simulation[32-36] to calculate the formation of hydrogen bonds (Table 1). As can be seen, almost all of the hydrogen bonds are Type I -OH···N hydrogen bond, further indicating that Type I -OH···N hydrogen bond is the dominant hydrogen bonds during polymerization. Moreover, the statistical results can also give the statistical length and length distribution of Type I -OH···N hydrogen bond (Fig. 3 a). The statistical lengths of P*p*C-a, P*p*C-ba and P*p*C-c calculated from Gauss Fit function are respectively 1.853, 1.722 and 1.692 Å. For the length distribution, the lengths of Type I -OH···N hydrogen bond for P*p*C-ba and P*p*C-c are mainly 1.6-1.8 Å, but those of P*p*C-a are 1.8-2.0 Å. These probably suggested that Type I -OH···N hydrogen bonds of P*p*C-ba and P*p*C-c were stronger than that of P*p*C-a. And as an evidence, P*p*C-a also exhibit the largest molecular weights, probably benefited from the weak Type I -OH···N hydrogen bond which may reduce the adjacent hydroxyl groups' charged densities and further hinder the polymerization.

To prove our hypothesis, we used Molecular Studio software[37] to calculate the charged densities. If no hydrogen bonds form, the adjacent hydroxyl groups' charged densities of P*p*C-a, P*p*C-ba and P*p*C-c are successively -0.064, -0.057 and -0.063, and changed to -0.056, -0.051 and -0.050 when Type I -OH···N hydrogen bonds formed (Fig. S5 and Fig. S6). This indicated that the charged densities decreased after formation of Type I -OH···N hydrogen bond. Since reactions on the *ortho*-position of phenol belong to electrophilic aromatic substitution, the decreased charged densities should be adverse to these reactions. That is, Type I -OH···N hydrogen bond decrease the adjacent hydroxyl groups' charged

densities and further block the high-degree polymerization (Scheme 1, Path a).

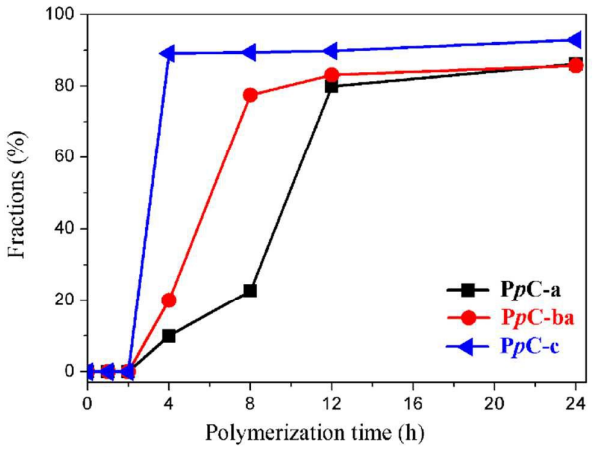


Fig. 2 The fractions of Type I -OH···N hydrogen bonds for P*p*C-a, P*p*C-ba and P*p*C-c after isothermal polymerization for different times.

Table 1 The quantities of hydrogen bonds of P*p*C-a, P*p*C-ba, P*p*C-c, P*p*C-a/PC, P*p*C-ba/PC and P*p*C-c/PC calculated by molecular dynamics (MD) simulation

Sample	P*p*C-a	P*p*C-ba	P*p*C-c	P*p*C-a/PC	P*p*C-ba/PC	P*p*C-c/PC
Type I [a]	23	27	24	19	20	25
Type II [b]	- [d]	- [d]	- [d]	7	4	3
-OH···O [c]	1	0	0	2	1	0

[a] Type I -OH···N hydrogen bond, [b] Type II -OH···N hydrogen bond, [c] -OH···O hydrogen bond, [d] inexistence.

As mentioned previously, this work also aims to gain the high-degree polymerization of benzoxazines. Because Type I -OH···N hydrogen bond blocks the polymerization, we attempted to improve the polymerization *via* controlling this hydrogen bonds. In the case of polybenzoxazines, the amount of hydrogen-bond acceptors is larger than that of donor. Due to the saturation property of hydrogen bonds, if additional stronger hydrogen-bond acceptors are introduced into benzoxazines' polymerization, Type I -OH···N hydrogen bond will be suppressed. The additional hydrogen-bond acceptor in this work is 4,4'-bipyridine. Then, we calculated the adjacent hydroxyl groups' charged densities after forming hydrogen bonds between 4,4'-bipyridine and -OH (denoted as Type II -OH···N hydrogen bond). The charged densities of P*p*C-a/PC, P*p*C-ba/PC and P*p*C-c/PC are -0.061, -0.053 and -0.057 (Fig. S7), respectively. Compared to the adjacent hydroxyl groups' charged densities without hydrogen bonds, a few decrease is observed and will block the polymerization a little.

To evaluate whether forming Type II -OH···N hydrogen bonds, the present work also uses molecular dynamics (MD) simulation to calculate the formation of hydrogen bonds in the presence of 4,4'-bipyridine (Table 1). The dominant hydrogen bonds are still Type I -OH···N hydrogen bond, however, Type II -OH···N hydrogen bonds are observed. Moreover, the length distributions of Type I -OH···N hydrogen bond also changed (Fig. 3 b). Although all the lengths of Type I -OH···N hydrogen bond mainly distribute in the range of 1.6-1.8 Å, the numbers of the hydrogen bonds distributed in the range of 1.6-1.8 Å and 1.8-2.0 Å alter. These suggested that the hydrogen bonds of polybenzoxazines can be changed and controlled through adding 4,4'-bipyridine.

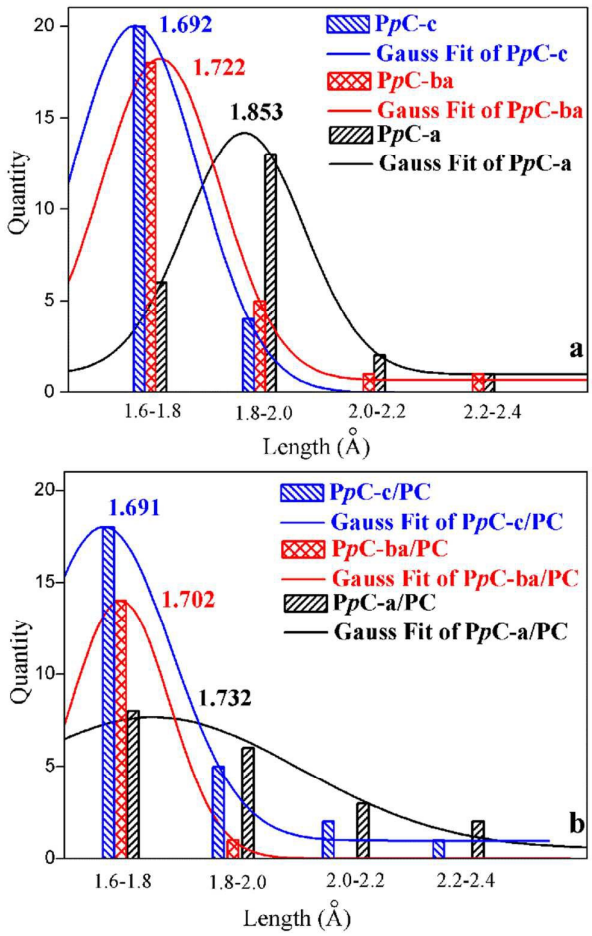


Fig. 3 The statistical lengths and length distributions of Type I -OH···N hydrogen bond for (a) P*p*C-a, P*p*C-ba and P*p*C-c, (b) P*p*C-a/PC, P*p*C-ba/PC and P*p*C-c/PC.

The formation of hydrogen bonds during polymerization in the presence of 4,4'-bipyridine were further confirmed by FTIR (Fig. S12). As can be seen from Fig. 4, Type I -OH···N hydrogen bond are still the dominant hydrogen bonds after polymerizing for a short time. For instance, the fractions of Type I -OH···N hydrogen bond of P*p*C-a/PC, P*p*C-ba/PC and P*p*C-c/PC are respectively 55.0%, 57.6% and 77.2%, while the sets of Type II -OH···N hydrogen bond are 34.9%, 42.4% and 22.8% after polymerizing for 24h. This further indicated that hydrogen bonds of polybenzoxazines are controlled by adding 4,4'-bipyridine. Since Type I -OH···N hydrogen bonds are averse to polymerization, the decrease in Type I -OH···N hydrogen

bonds will be benefit for improving the polymerization. In the presence of 4,4'-bipyridine, conversions (α) and molecular weights ($\overline{M_n}$) of benzoxazines under isothermal polymerization at 160 °C (Fig. 5) are probed. After introducing 4,4'-bipyridine, all of the $\overline{M_n}$ increased. Both the improvement of polymerization and the reactions between benzoxazines and 4,4'-bipyridine can increase the $\overline{M_n}$, but no obvious signals or peaks about 4,4'-bipyridine were observed in FTIR (Fig. S1) and ^{1}H NMR (Fig. S2) after precipitating in methanol suggested that the increased $\overline{M_n}$ should be attributed to the improvement of polymerization. Compared to P*p*C-a, the $\overline{M_n}$ of P*p*C-a/P significantly increased to 1934 and 3408 D after polymerizing for 12h and 24h, respectively. This increase is probably attributed to the decrease in Type I -OH···N hydrogen bond and other forms of phenolic hydroxyl group (-OH···O formation hydrogen bond, the total fraction is ~10%). The $\overline{M_n}$ of P*p*C-ba/P increased slightly after adding 4,4'-bipyridine, for example, the $\overline{M_n}$ of P*p*C-ba and P*p*C-ba/P were respectively 770 and 1554 D after polymerizing for 24 h. However, a little increase was observed in P*p*C-c/P (increased from 725 D to1021 D). These differences were in accordance with the variety of hydrogen bonds. The results suggested that high-degree polymerization of benzoxazines can be gained *via* controlling hydrogen bonds (Scheme 1, Path b), and also further supported that Type I -OH···N hydrogen bond blocked the high-degree polymerization of benzoxazines.

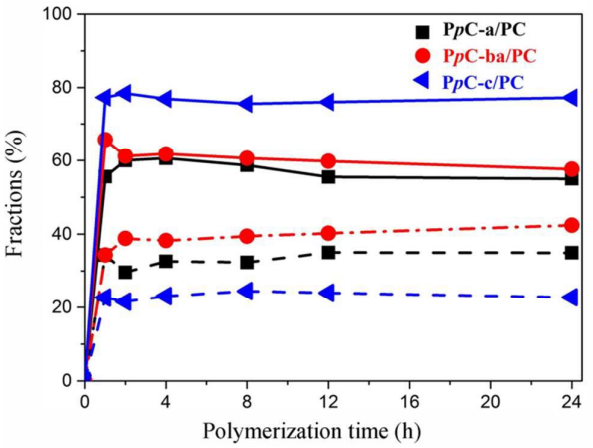


Fig. 4 The fractions of Type I -OH···N hydrogen bonds (solid line) and Type II -OH···N hydrogen bond (dash line) for P*p*C-a/PC, P*p*C-ba/PC and P*p*C-c/PC after isothermal polymerization for different time.

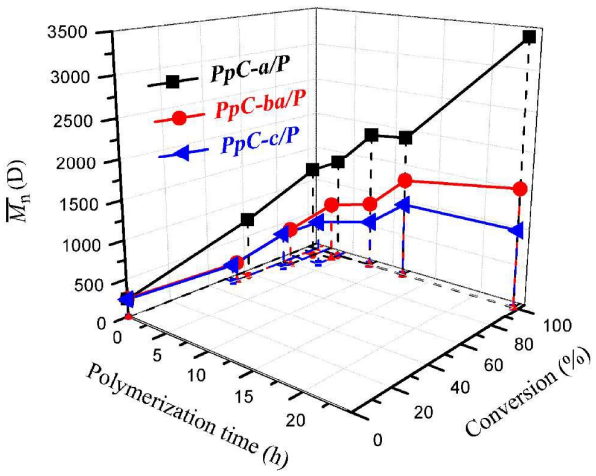


Fig. 5 The conversions (α) and molecular weights ($\overline{M_n}$) of P*p*C-a/P, P*p*C-ba/P and P*p*C-c/P after polymerizing for different time at 160 °C.

Conclusions

In summary, this work invested which blocked high-degree polymerization of benzoxazines and which resulted in the low crosslink density of polybenzoxazines. -OH···N hydrogen bond of polybenzoxazines (Type I -OH···N hydrogen bond) blocked high-degree polymerization and resulted in the low crosslink density by decreasing the charge densities of corresponding hydroxyl groups on phenols. To gain high-degree polymerization of benzoxazines, additional hydrogen-bonds acceptor, 4,4'-bipyridine, was introduced to control the formation of hydrogen bonds. Since the formation of Type I -OH···N hydrogen bonds were suppressed, the polymerization was improved and higher molecular weights of polybenzoxazines were gained. These revealed that Type I -OH···N hydrogen bond produced the low crosslinked polybenzoxazines and crosslink density can be increased *via* controlling hydrogen bonds. This finding is anticipated to help researchers understand why polybenzoxazines exhibit low crosslink density and how to increase crosslink density.

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Effect of hydrogen bonds on the polymerization of benzoxazines: influence and control

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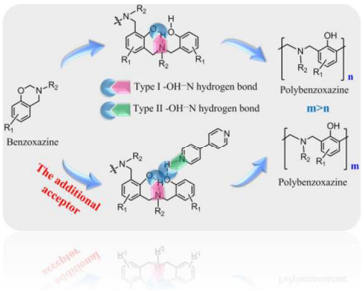

Graphical Abstract

Textual abstract: Type I -OH···N hydrogen bonds blocked high-degree polymerization of benzoxazines and controlling them by introducing additional hydrogen-bonds acceptors can afford high-degree polymerization.