Post-polymerization modification of polybenzoxazines by boronic acids supported by B–N interactions

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COMMUNICATION

Post-polymerization modification of polybenzoxazines by boronic acids supported by B–N interactions†

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Polybenzoxazines (PBZs) were modified using the reactivity of their inherent bis(2-hydroxybenzyl)amine (BHBA) units toward boronic acids, $RB(OH)_2$. These condensation reactions led to changes in the properties of the original PBZs without changing their shape and thermal stability.

Polybenzoxazines (PBZs) are thermosetting resins that have recently been obtained from the ring-opening polymerization (ROP) of the corresponding cyclic monomers, benzoxazines.[1,2] They are classified as phenolic resins that exhibit good thermal properties as well as flame-retarding properties comparable to those of conventional phenolic resins. Moreover, they exhibit excellent dimensional stability, a low propensity to absorb water, and good dielectric properties, all of which are characteristics superior to those of conventional phenolic resins.[3–5] Additionally, because of the molecular design of benzoxazines is characterized by a high degree of freedom due to their structural diversity, some fascinating researches of PBZs have been reported recently.[6–8] Such molecular design flexibility enable PBZs to have found widespread applications as e.g., matrices for carbon-fiber-reinforced plastics, electronic products, and adhesives.[9–13]

To expand the range of applications of PBZs, modifications by copolymerization with other monomers have been reported.[14–19] However, these pre-polymerization modifications may negatively affect some properties of the final polymer materials. Beltran *et al*. have reported a direct sulfonation of thermally cross-linked electrospun PBZ nanofibers;[20] however, this is, to the best of our knowledge, the only example of the post-polymerization modification of PBZs, despite the fact that various post-polymerization modification methods for polymers in general have already been reported.[21] Thus, post-polymerization modification methods have to be further developed in order to expand the applications of PBZs.

Previously, we have reported the direct modification of amine-cured epoxy resins with boronic acids, $RB(OH)_2$.[22–23] This modification method is based on the dynamic formation of dioxazaborocane from diethanolamine units in amine-cured epoxy resins and boronic-acid derivatives using the reaction that yields boronates from boronic acids and diols.[24–26] Diethanolamine units in the amine-cured epoxy resins were treated with phenylboronic acid with a dye, a linear polymer with boronic-acid pendants, and cross-linked polymers containing boronic-acid groups, resulting in a change of color, a coating of the epoxy resins, and adhesion between resins, respectively. Although such modifications and functionalization of cured epoxy resins had been considered challenging, this method using boronic acids is able to accomplish them.

In the present study, we focused on bis(2-hydroxybenzyl)amine (BHBA) units generated from the ROP of benzoxazine for the controlled modification of PBZs. The formation of dioxazaborecine (DOAB) moieties from BHBA and boronic-acid derivatives has been reported for the reaction of small molecules.[27] Based on this reaction, our effort was aimed at the post-polymerization modification of PBZs by various boronic-acid derivatives (Fig. 1). Moreover, we expected that modifications without losing the functional properties of the original PBZs is feasible because the present method exploits intrinsic BHBA units in the polymer main chain, which are formed by the ROP of the benzoxazines.

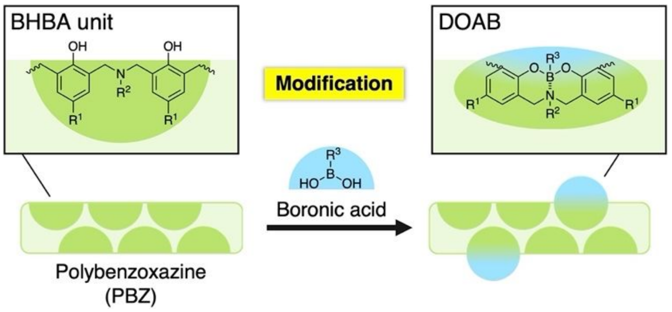

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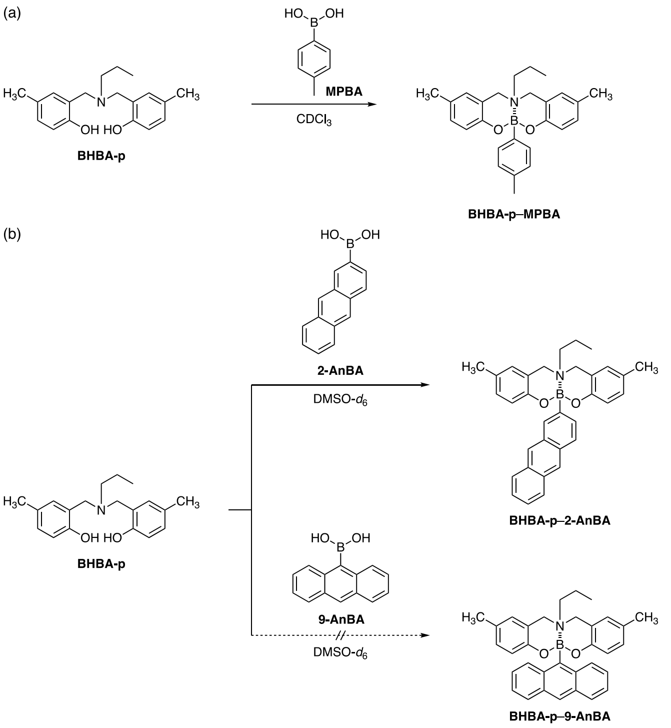
Fig. 1. Schematic illustration of the post-curing modification of PBZs by boronic acids, $RB(OH)_2$.

Results and discussion

Model reaction

Initially, the reactivity of the BHBA moieties with a boronic acid was investigated. In one of our previous studies, we have reported that the intramolecular interactions between nitrogen and boron atoms is weak when aromatic amines are used.[22] Thus, the *N*-propyl derivative (**BHBA-p**) was used in the condensation reaction with an equimolar amount of 4-methylphenylboronic acid (**MPBA**) in $CDCl_3$ (Scheme 1a). The formation of the DOAB moiety was confirmed by ^1H and ^{13}C NMR spectroscopy as well as fast atom bombardment (FAB) mass spectrometry (Figs. S5–S9). It should be noted here that the BHBA-forming reaction proceeded quantitatively, regardless of the presence of the anhydride boroxine.[28]

To investigate whether the reactivity of the BHBA moieties changes depending on the structure of the boronic acids, we tested structural isomers of anthraceneboronic acid, i.e., 2-anthraceneboronic acid (**2-AnBA**) and 9-anthraceneboronic acid (**9-AnBA**) (Scheme 1b). The ^1H NMR spectra of the equimolar mixture of **BHBA-p** and anthraceneboronic acids indicated that the formation of the DOAB moiety occurred only in the case of **2-AnBA** (Figs. S10–S15). Furthermore, a change in the fluorescence properties, such as a decrease in the fluorescence intensity at 419 nm and a shift of the emission band from 441 nm to 438 nm, was observed only for the mixture of **BHBA-p** and **2-AnBA** (Fig. S16). These results indicate that the formation of the DOAB structure via intramolecular B–N interactions occurred, while simultaneously, the hybridization of the boron atom in **2-AnBA** changes from sp^2 to sp^3.[29–30] On the other hand, spectral changes were not observed when **9-AnBA** was used. This result indicates that sterically hindered boronic acids such as **9-AnBA** are not suited for the reaction with **BHBA-p**.[31] These results suggest that sterically unhindered boronic acids are the most appropriate modifiers for PBZs.



Scheme 1. Reactions of **BHBA-p** and (a) 4-methylphenylboronic acid (**MPBA**) as well as (b) 2-anthraceneboronic acid (**2-AnBA**) and 9-anthraceneboronic acid (**9-AnBA**).

The hydrolytic stability of **BHBA-p–MPBA**, and dioxazaborocane formed with diethanolamine and **MPBA**[22] which we previously reported were investigated. As reported by Jing's group,[32] we dissolved each complex in DMSO-d_6 with 20 equivalent water, and their hydrolysis stability were evaluated by ^1H NMR. The hydrolysis percentage of **BHBA-p–MPBA** and dioxazaborocane were 2.4% and 31.6% when the equilibrium reached, respectively. Compared to the hydrolysis percentage of the complex reported by Jing's group (15.8%), nitrogen-coordinating cyclic boronic diester compounds, and dioxazaborocane (31.6%), **BHBA-p–MPBA** showed higher hydrolysis stability (2.4%). Furthermore, the hydrolysis equilibrium constant (K_{eq} = ([boronic acid] [donor])/[complex] $[H_2O]^2$) of **BHBA-p–MPBA** (3.36×10^{-5} L·mol^{-1}) was estimated based on the ^1H NMR spectrum. This value is much lower than that of dioxazaborocane (1.13×10^{-2} L·mol^{-1}). Thus, the DOAB skeleton is expected to be stronger than the dioxazaborocane framework of the previously reported epoxy system. These results indicate that significantly high stability of DOAB is applicable to the modification in polymeric systems.

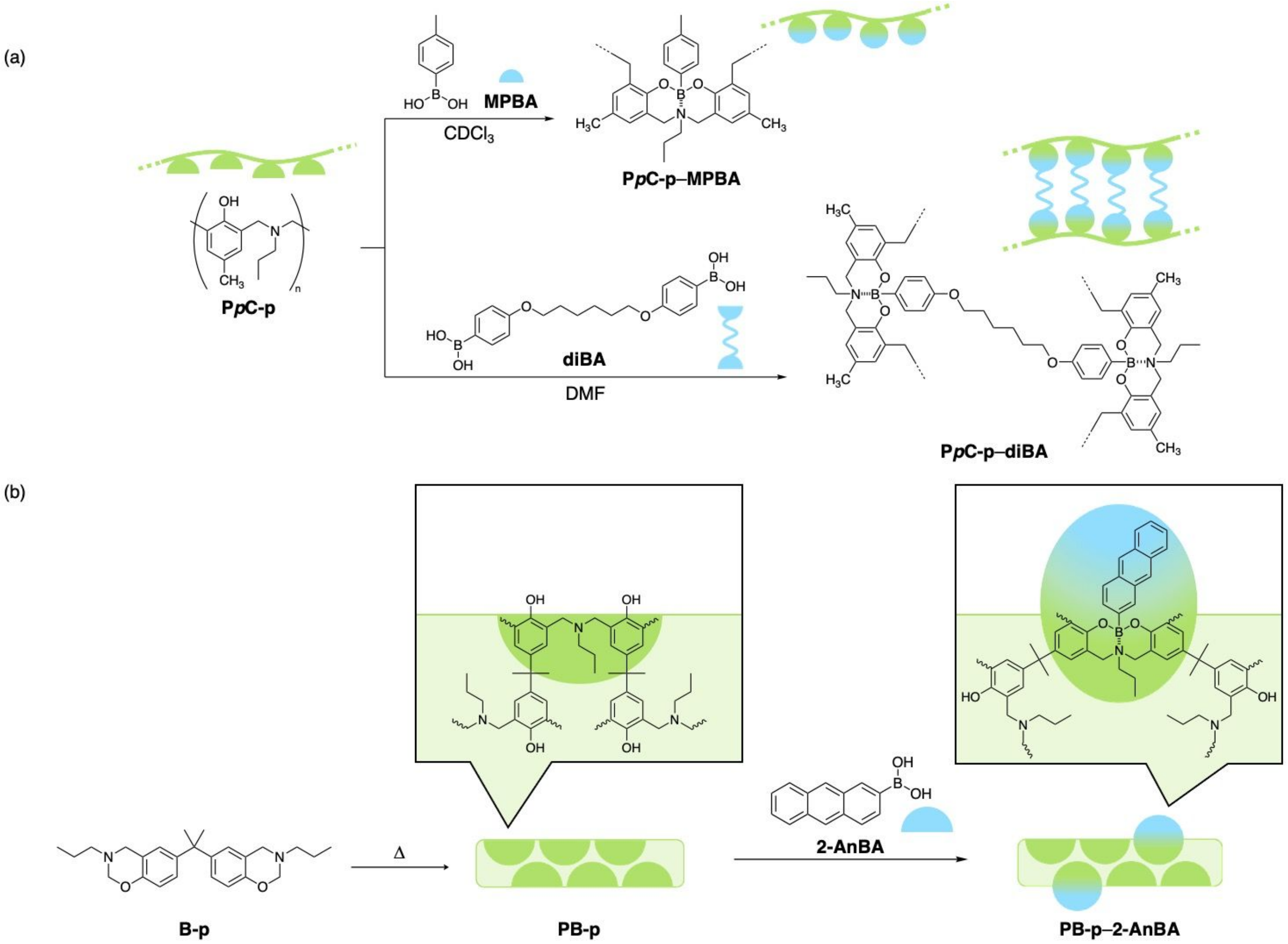
To assess the thermal stability of the DOAB moiety, **BHBA-p–MPBA** was heated from 25 °C to 100 °C and monitored by ^1H NMR spectroscopy (Fig. S17). The decomposition of the DOAB moiety as a function of the reaction time at each temperature is shown in Fig. S18. The binding constant calculated based on the peak intensity in the ^1H NMR spectra[33] decreased only slightly as a function of temperature, which is much higher than that of the previously reported dioxazaborocane (Fig. S19).[22] It should be noted that this value of binding constant is not accurate because certain amount of water was not considered in the equation we used. Here, we referred this value in order to compare the stability with that of dioxazaborocane we previously reported. This result confirms the high thermal stability of the DOAB moiety.

Polymer reaction

Subsequently, we applied this reaction to the modification of BHBA moieties in polymeric systems with boronic acids (Scheme 2a). For that purpose, a linear polybenzoxazine (**P*p*C-p**) was synthesized via the thermally induced polymerization of monofunctional benzoxazine (***p*C-p**) prepared from *p*-cresol, propylamine, and paraformaldehyde (Scheme S1, Fig. S1 and Fig. S2).[34] When **P*p*C-p** and **MPBA** were mixed in $CDCl_3$, new signals corresponding to **P*p*C-p–MPBA** were observed in the ^1H NMR spectrum (Fig. 2). Additionally, diffusion-ordered spectroscopy (DOSY) measurements[35] were carried out to confirm the change in hydrodynamic volume before and after the post-polymerization modification. The mixture of **P*p*C-p** and **MPBA** exhibited almost exclusively a single diffusion coefficient (Fig. S20), implying that **MPBA** reacted with the BHBA units in the polymer chain. Furthermore, the modification of the polymer chain with **MPBA** to generate **P*p*C-p–MPBA** was corroborated by the newly observed diffusion coefficient, which is different from that of **P*p*C-p**. ^{11}B NMR data also supporting the binding reaction (Figure S21). Based on these results, it is feasible to conclude that **MPBA** was introduced into the **P*p*C-p** polymer via the formation of DOAB moieties.

Gelation

Subsequently, we attempted a cross-linking reaction between the linear PBZ chains using a bifunctional diboronic acid. For this purpose, ((hexane-1,5-diylbis(oxy))bis(4,1-phenylene)diboronic acid (**diBA**) was synthesized and characterized spectroscopically (Schemes S2 and S3 as well as Figs. S22–S29). **P*p*C-p** and **diBA** were mixed in DMF at room temperature (Scheme 2a), and although gelation was not observed immediately upon mixing, the viscosity of the reaction mixture increased after adding molecular sieves 4Å, and a gel of **P*p*C-p–diBA** was obtained after 24 hours (Fig. 3). This result supports the notion that bifunctional boronic acids such as **diBA** work as cross-linkers in



Scheme 2. Reactions of (a) **P*p*C-p** with **MPBA** (top) and **diBA** (bottom); (b) **PB-p** with **2-AnBA**.

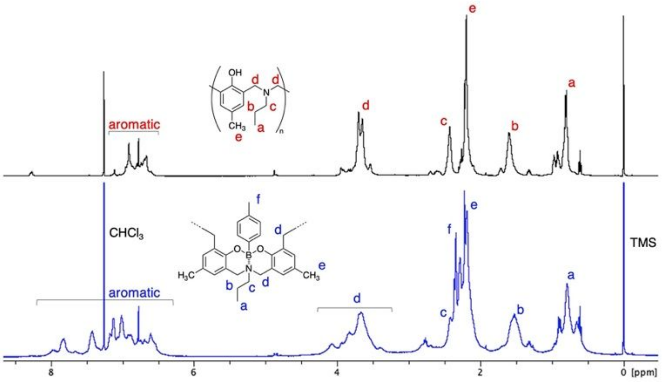


Fig. 2. ^{1}H NMR spectra of **P*p*C-p** (black) and **P*p*C-p–MPBA** (blue) in $CDCl_3$ at 25 °C.

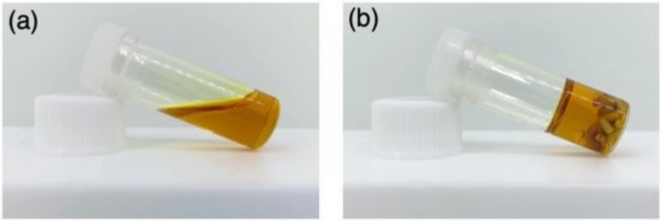


Fig. 3. Photographs of a solution of **P*p*C-p** and **diBA** (a) before and (b) after the addition of molecular sieves 4Å.

the reaction with the BHBA units in the polymer chains. It also suggests that the amount of water has a significant effect on the formation of the DOAB moieties in the present polymer system.

Modification of PBZ by a fluorescent boronic acid

Encouraged by the results of the model and homogeneous reactions, we attempted a modification of the cross-linked PBZ that was obtained from the polymerization of a bifunctional benzoxazine monomer (Scheme 2b). The bifunctional benzoxazine prepared by the reaction of bisphenol A, propylamine, and paraformaldehyde was cured under bulk conditions as previously reported (Scheme S4, Fig. S3 and Fig. S4).[34] After heating to 150 °C under a nitrogen atmosphere, a cross-linked PBZ (**PB-p**) with high transparency was obtained (Fig. S30). With this condition, we obtained loosely cured **PB-p** in which exothermic peak derived from polymerization is still confirmed in the DSC profiles (Fig. S4). Fully cured **PB-p** was also obtained by stepwise thermal treatment (140 °C / 2 h, 160 °C / 2 h, 180 °C / 2 h, 200 °C / 15 h), in which exothermic peak has not confirmed (Fig. S33). With loosely cured **PB-p**, we confirmed the reaction progress between the BHBA moieties in the PBZ and **2-AnBA** or **9-AnBA** by measuring their fluorescence. Crushed samples of **PB-p** were immersed in a tetrahydrofuran (THF) solution of the anthraceneboronic acids (5.0 × 10^{-2} M). After 24 hours, samples were removed, washed three times with THF, and dried under ambient conditions. As shown in Fig. 4, only the sample immersed in the solution of **2-AnBA** exhibited strong fluorescence. The difference in fluorescence emission of the obtained samples also manifests in their fluorescence emission spectra (Fig. S31). These results are consistent with the results described in the model reactions, i.e., **9-AnBA** does not react, and only **2-AnBA** forms a complex with the BHBA moieties. Interestingly, we confirmed that when **2-AnBA** formed a complex with a small molecule, the shape of its fluorescence spectrum changed without any peak shift (Fig. S32, blue), on the other hand, when it formed a complex with a polymer, its fluorescence spectrum shifted to the long-wavelength side (Fig. S32, red and purple). This peak shift might be attributed to adjacent anthracene units on polymer chain.

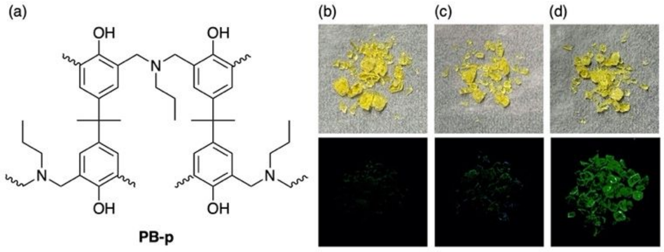


Fig. 4. (a) Chemical structure of **PB-p**. Photographs under irradiation from visible (top) and UV light (bottom) of **PB-p**s treated with (b) THF, (c) **9-AnBA** in THF, and (d) **2-AnBA** in THF.

In the case of non-crushed circular films of the **PB-p**, modification was conducted by immersion in a 1,4-dioxane/THF (2/1, v/v) solution of **2-AnBA** (2.0 × 10^{-2} M) for 48 hours. The obtained circular film showed fluorescence without significant change of shape (Fig. 5). Based on the discussion above, we concluded that the BHBA units in **PB-p** react with the boronic acid. On the other hand, modification of fully cured **PB-p** was not achieved under the same condition. However, with the condition conducted by immersion in a THF solution of **2-AnBA** for 48 h at 50 °C, the obtained film showed weak fluorescence (Fig. S34). Although the modification reaction with boronic acid became difficult as the cross-link density increased, BHBA units can be used as the scaffold toward the modification of PBZ.

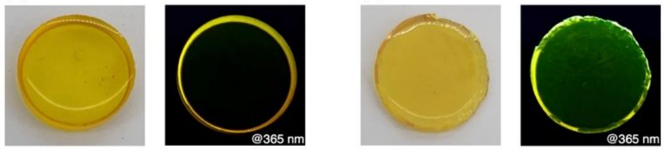


Fig. 5. Photographs under irradiation from visible (left) and UV light (right) of (a) **PB-p** and (b) **PB-p** treated with **2-AnBA** in 1,4-dioxane/THF (2/1, v/v).

Thermal stability of the modified PB-p

The thermal stability of the modified **PB-p** was compared to the non-modified **PB-p** to evaluate the influence of the modification with boronic acid on the thermal stability of the PBZ. The thermogravimetric analysis (TGA) of the modified and non-modified sample showed almost the same thermal resistance with an onset temperature of degradation at approximately 270 °C (Fig. 6). This result supports the notion that the modification occurs without affecting the heat tolerance of original PBZ.

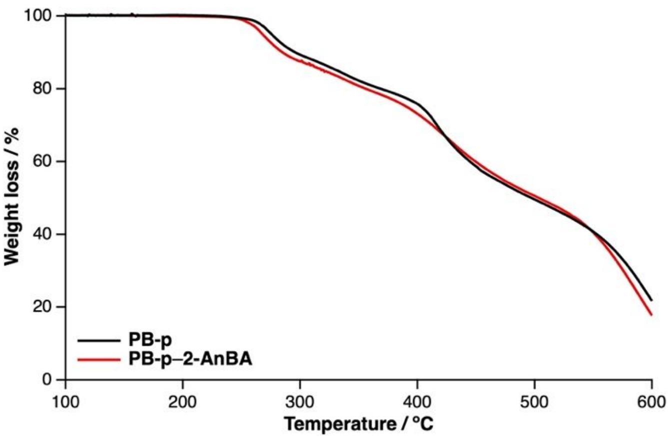


Fig. 6. TGA curves of **PB-p** (black) and **PB-p–2-AnBA** (red).

Conclusions

In conclusion, we have shown the concept of an effective method for the post-polymerization modification of polybenzoxazines (PBZs), based on the intrinsic reactivity of the BHBA moieties in PBZs toward boronic acids to form dioxazaborecine (DOAB) moieties, which was monitored by NMR spectroscopy. Using this new method, we were able to modify linear PBZs and to cross-link PBZs with mono- and bifunctional boronic acids, respectively. A reaction between the BHBA units in a PBZ and a fluorescent boronic acid resulted in a change of the fluorescence properties of the original cross-linked PBZ. Modification of fully cured PBZ is still challenging, however, this method has the potential of a promising technique to modify and functionalize existing PBZs. Given the diversity of boronic acids, the present method can be expected to serve as a versatile tool for the modification of PBZs that will hopefully lead to new applications of the thus obtained functionalized polymers.

Conflicts of interest

There are no potential conflicts of interest to declare.

Acknowledgements

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