

Understanding the surface properties of polybenzoxazines: Interaction of polybenzoxazine model compounds with metal ions and water

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ABSTRACT: The structure of polybenzoxazines (and their properties) is mainly defined by the existence of intra- and intermolecular hydrogen bonds. The effect of different substituents present in the phenolic ring of polybenzoxazines can modulate these intermolecular forces and the interaction with other materials, such as metals. To extend this knowledge, a series of structure-controlled polybenzoxazines and polybenzoxazine model compounds have been synthesized. The interactions with different metal ions have been investigated using UV–vis and NMR analysis. Association constants have been estimated by UV–vis titration method and the effect of the presence of different substituents in the aromatic ring has been established. Water contact angles have also been measured. The different techniques give us information about the inner hydrogen bonding structure. Cyano group, present as substituent in polybenzoxazine compounds, acts as an additional coordination point towards metal ions and water. Our findings should allow modulating the adhesion and other surface properties of the benzoxazine-derived polymers by playing with the properties of the substituents and their structure (phenoxy/phenolic). © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44099.

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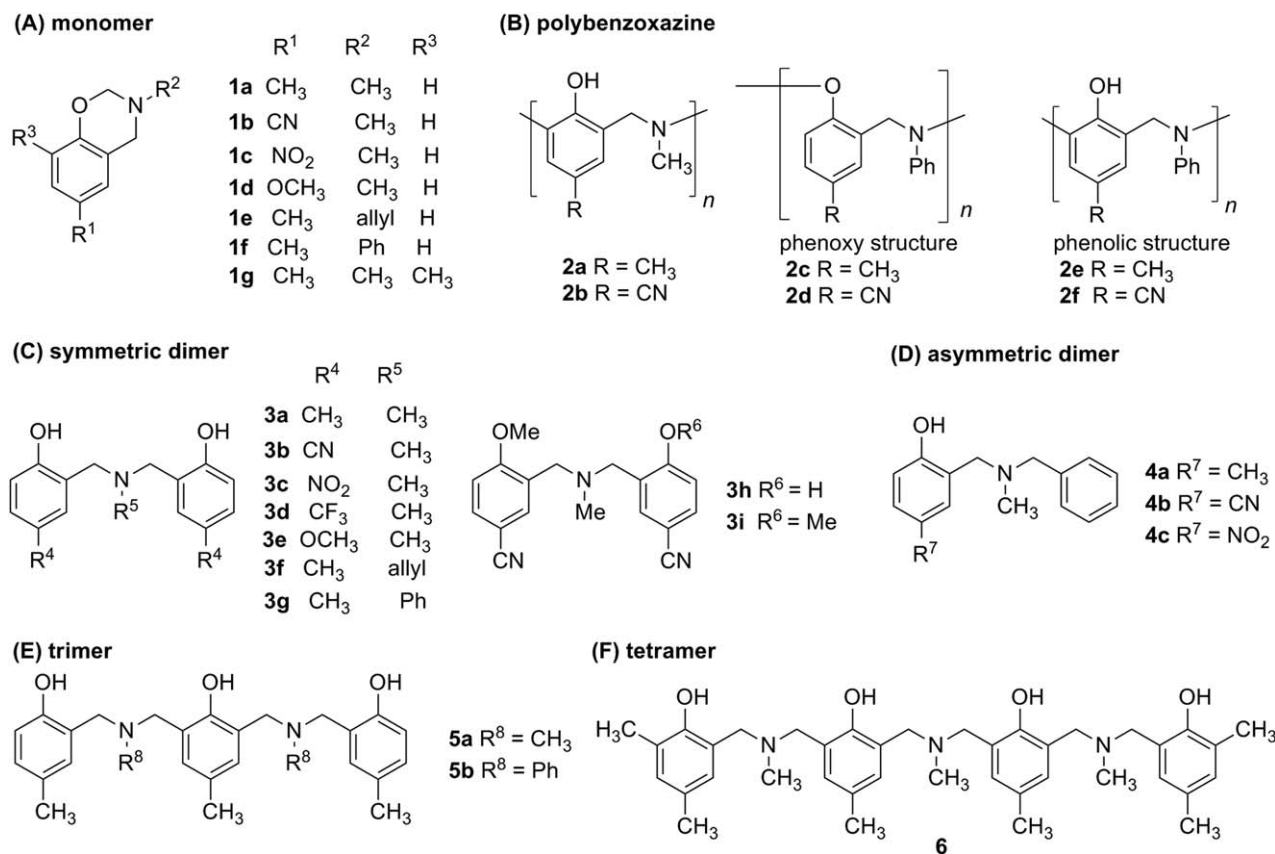
INTRODUCTION

Polybenzoxazines are a young class of phenolic resins obtained by the ring-opening polymerization of benzoxazine monomers.^{1,2} They have been found to exhibit excellent mechanical properties,^{3,4} near-zero shrinkage or volumetric expansion upon polymerization,⁵ high char yield,⁴ low water absorption,³ and good dielectric properties,⁶ which make them potential candidates for high performance applications. However, one of the main shortcomings of polybenzoxazines is their brittleness and low process ability. Their combination with other polymeric and inorganic materials is considered to be a good and effective solution.^{1,2} The properties of these multicomponent materials are to a great extent dependent on the interfacial interaction of the phases across the interphase. The unusual properties of polybenzoxazines described earlier have been attributed to their complex hydrogen bond pattern. Almost all known forms of hydrogen bonds, both inter- and intramolecular are possible in polybenzoxazines. Of particular interest are the very stable six-membered intramolecular hydrogen bonds formed between the phenolic hydrogens and the amine nitrogens. These intramolecular hydrogen bonds have been proposed as responsible of the

hydrophobicity, low dielectric constant, high char yield, and high modulus of polybenzoxazines.¹ However, as a drawback, these very strong intramolecular hydrogen bonds reduce their surface energy, making in many cases their interaction with other materials weak. So a good understanding of the surface properties of standard polybenzoxazines and polybenzoxazines modified by introducing different polar substituents in the phenolic ring, and their interaction with other materials, such as metals or water is very important. To this end, although a few reports have appeared on the interaction of benzoxazines or polybenzoxazines with various metal ions,^{1,7–9} and even in one case, these materials have been proposed for the removal of metal salts from water,¹⁰ there is still a need for further investigation, especially with the aim of improving the interaction of polybenzoxazines with other materials without altering the inner hydrogen bond structure that provides their excellent mechanical properties. Considering the difficulties of analyzing the structure of polybenzoxazine, we focus on studying the interaction of model compounds benzoxazine “dimers,” “trimers,” and a “tetramer” (Scheme 1) with various metal ions and water. In this work, attempts on estimating the association constants for

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Scheme 1. Prepared model molecules and polymers derived from benzoxazines.

various model compounds–metal ion complexes were carried out and values are described for the case of zinc cation. The interaction of various polybenzoxazines and model compounds with water was also investigated by comparing the water sessile drop contact angles of glass surfaces covered by them. Our aim here would be to understand how to reduce the hydrophobicity of polybenzoxazines keeping the rest of their excellent properties, hydrophobicity being a measure for intermolecular hydrogen bonds and other intermolecular polar interactions. Data from these studies on polybenzoxazines and polybenzoxazine model compounds can significantly contribute to the understanding of adhesion and other surface properties of polybenzoxazines. Indeed, the differences between “phenoxy” and “phenolic” structures in polymers,¹ and the effect of additional polar functional groups on the interacting ability of polymers and model compounds are discussed.

EXPERIMENTAL

Materials and Measurements

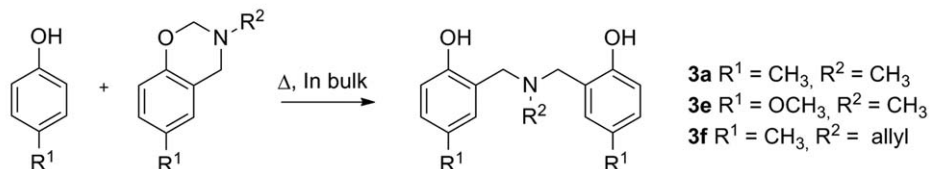
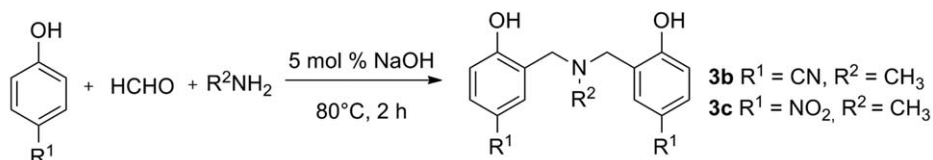
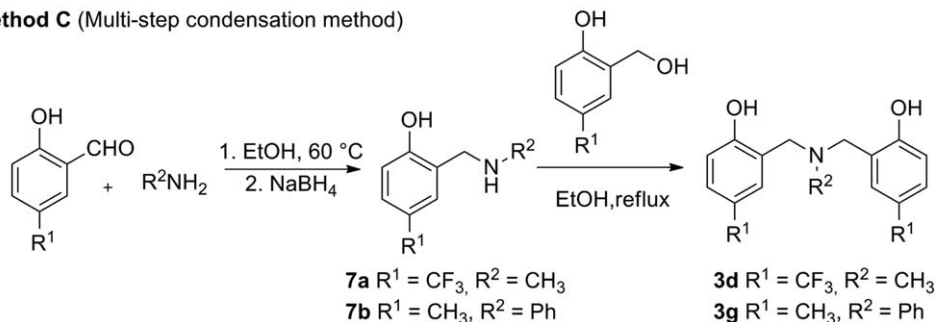
All chemicals were purchased from Aldrich Chemical Co. and used without further purification. Column chromatographies have been performed in silica gel purchased from Scharlau (Silica Gel 60, 230–440 mesh). The formaldehyde was 37 wt % in water, and the methylamine was 40 wt % in water. NMR spectra were taken on a Bruker AM-360 (360 MHz). Chemical shift were reported in parts per million relative to TMS as an internal standard ($\delta_{\text{TMS}} = 0$) for NMR spectra (digital resolution 0.26 Hz/point for ¹H-NMR and 1.32 Hz/point for ¹³C-NMR).

The solvents for NMR measurement were deuterated DMSO, deuterated methanol, or deuterated chloroform. UV–vis absorbance data were obtained on Hewlett-Packard 8453 (resolution 1 nm). Infrared spectra were recorded on Bruker Tensor 27 instrument equipped with an ATR Golden Gate cell and a diamond window (digital resolution 4 cm⁻¹) and Nicolet FT-IR 510 ZDX (KBr). Elemental analysis or high resolution mass spectrometry (HR-ESI-MS, Bruker MicroTOF-Q) have been used to confirm the structures of new synthesized compounds.

Synthesis of Benzoxazine Monomers and Polybenzoxazines

As shown in Scheme 1, benzoxazine monomers **1** were prepared by using phenol, formaldehyde, and amine in the ratio of 1:2:1. The procedure was described by Ishida¹¹ or Ronda *et al.*¹² Purification was finished by column chromatography. Benzoxazine monomers **1a**,¹³ **1f**,¹² and **1g**¹⁴ were prepared according to the literature. The polymers, **2**, with different structures were obtained by controlling the curing temperature and time according to our previously reported studies.¹⁵ Benzoxazine monomer used for preparing polymers **2d** and **2f**, was synthesized following the literature.¹⁶

Experimental conditions and spectroscopic data of new, and previously not fully described benzoxazine monomers, 3-methyl-6-cyano-3,4-dihydro-2H-1,3-benzoxazine (**1b**), 3-methyl-6-nitro-3,4-dihydro-2H-1,3-benzoxazine (**1c**), 3-methyl-6-methoxy-3,4-dihydro-2H-1,3-benzoxazine (**1d**),¹⁷ and 3-allyl-6-methyl-3,4-dihydro-2H-1,3-benzoxazine (**1e**),¹⁸ are gathered in the SI.

Method A (Benzoxazine-phenol condensation method)**Method B** (Mannich reaction method)**Method C** (Multi-step condensation method)

Scheme 2. Synthesis of symmetric “dimers.”

Synthesis of Symmetric Benzoxazine “Dimers”

Various “dimers” were prepared following three general synthetic methods depicted in Scheme 2. Compounds **3a**⁷ and **7b**¹⁹ have been described in previous papers and obtained in similar yields.

Method A²⁰. Dimers were prepared from ring-opening reactions of the corresponding benzoxazine monomers with phenols. The stoichiometric mixture of benzoxazine monomer and the corresponding phenol was heated in bulk at 100 °C for 1 h. The resulting mixture was directly recrystallized from Et₂O to give the desired product.

Experimental conditions and spectroscopic data of new benzoxazine “dimers,” *N,N*-bis(5-methoxy-2-hydroxybenzyl)methylamine (**3e**),²¹ and *N,N*-bis(5-methyl-2-hydroxybenzyl)allylamine (**3f**), synthesized by this method are gathered in the SI.

Method B¹⁴. Dimers were synthesized from Mannich reaction. The modified procedure was described as following: a solution of formalin (37% in H₂O, 0.3 mL, 4 mmol), phenol (4 mmol), and 5 mol % NaOH was stirred in ethyl acetate (5 mL). After stirring for 10 min at room temperature, methyl amine (40% in H₂O, 0.17 mL, 2 mmol) was added. Then the mixture was stirred at 80 °C for 3 h. After cooling to room temperature, ethyl acetate in the mixture was carefully removed by rotary evaporator and the residue was filtered. The filter cake was collected, washed with Et₂O three times and dried under vacuum.

Spectroscopic data of new, and previously not fully described benzoxazine “dimers,” *N,N*-bis(5-cyano-2-hydroxybenzyl)methylamine

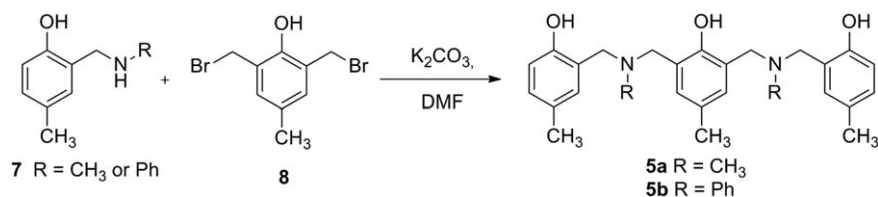
(**3b**), and *N,N*-bis(5-nitro-2-hydroxybenzyl)methylamine (**3c**) synthesized by this method, are gathered in the SI.

Method C²². The typical procedures are as following: (1) 2-hydroxy-5-methyl-benzaldehyde (2.72 g, 20 mmol) was added slowly to a solution of aniline (1.86 g, 20 mmol) in EtOH (20 mL). The mixture was stirred at 60 °C and the reaction was monitored by TLC. After completion and cooling to room temperature, NaBH₄ (380 mg, 10 mmol) was added in small portions. When the reduction was complete, the reaction mixture was extracted with dichloromethane, washed with water three times, dried over anhydrous Na₂SO₄ and concentrated to dryness to give a white solid **7b** (4.09 g, 96%). It was directly used in the next step without further purification. (2) *N*-(2-hydroxybenzyl-5-methyl)aniline (**7b**) (2.13 g, 10 mol) was added into a solution of salicyl alcohol (1.38 g, 10 mol) in 50 mL EtOH. The mixture was refluxed for 12 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane, washed with water three times, dried over anhydrous Na₂SO₄ and concentrated to dryness. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate (5:1) as the eluent. An analytical sample of **3g** was recrystallized from Et₂O.

Spectroscopic data of new, and previously not fully described benzoxazine “dimers,” *N,N*-bis(5-methyl-2-hydroxybenzyl)aniline (**3g**),²³ *N*-(2-hydroxybenzyl-5-trifluoromethyl)aniline (**7a**), *N,N*-bis(5-trifluoromethyl-2-hydroxybenzyl)methylamine (**3d**), synthesized by this method, are gathered in the SI.

Synthesis of Asymmetric Benzoxazine “Dimers”

The asymmetric model “dimers” (**4a**, **4b**, and **4c**) were synthesized according to the literature.^{24,25} Phenol, paraformaldehyde,



Scheme 3. Synthesis of “trimmers.”

and *N*-methylbenzylamine in the ratio of 1:1:1 were reacted in bulk at 100 °C for 1 h. The mixture was then dissolved in chloroform, washed several times with distilled water, and dried over anhydrous sodium sulfate. After removing the solvent, the resulting residue was purified by column chromatography (Hexane/EtOAc 10/1, 6/1, and 3/1, respectively).

Synthesis of Benzoxazine “Trimers” and “Tetramer”

The preparation of model “trimers” is shown in Scheme 3. Dibromide **8**²⁶ (294 mg, 1 mmol) was added to a stirred solution of amine **7** (2 mmol) and K₂CO₃ (552 mg, 4 mmol) in 10 mL DMF. The mixture was reacted at room temperature for 12 h. And then the reaction mixture was extracted with dichloromethane, washed with water, dried over anhydrous Na₂SO₄. The residual products were purified by column chromatography on silica gel using hexane/ethyl acetate (3:1) as the eluent. The model “tetramer” **6** was synthesized by method A as above (Scheme 2), but using monomer **1g** and dimer **3a** refluxed in chloroform for 24 h; product was purified by column chromatography using hexane/ethyl acetate (4:1) as the eluent.^{27,28} Purification details and spectroscopic data of new benzoxazine “trimers,” 2,6-bis[*N*-(5-methyl-2-hydroxybenzyl)-*N*-methyl-amino-methyl]-*p*-cresol (**5a**), and 2,6-bis[*N*-(5-methyl-2-hydroxybenzyl)-*N*-phenyl-amino-methyl]-*p*-cresol (**5b**), synthesized by this method, are gathered in the SI.

Synthesis of “Methylated Dimers”

To a stirred solution of dimer **3b** (294 mg, 1 mmol) dissolved in DMF (10 mL) was added K₂CO₃ (414 mg, 3 mmol) at room temperature for 10 min. Methyl iodide (355 mg, 2.5 mmol) was added dropwise, and then the mixture was stirred for 1 h. The reaction mixture was extracted with dichloromethane, washed with 10% NaOH and brine, and then dried over anhydrous Na₂SO₄. The residual products were subjected to column chromatography on silica gel using hexane/ethyl acetate (2:1) as the eluent to give methylated dimer **3h** and **3i**.

Spectroscopic data of new benzoxazine “methylated dimers,” *N*-(5-cyano-2-methoxybenzyl)-*N*-(5-cyano-2-methoxybenzyl)methylamine (**3h**), *N,N*-bis(5-cyano-2-methoxybenzyl)methylamine (**3i**), synthesized by this method, are gathered in the SI.

Typical Procedures for the Evaluation of Association Constants K_a by UV–Vis Titration.²⁹

Typical procedures consist of several steps: The concentration of each model compound solution in methanol was adjusted to obtain ~1 UV absorbance unit at the wavelength of about 280 nm as observed by UV spectroscopy: 1.65×10^{-4} M (**3a**, **3d**, **3e**, **3f**, **4c**, **5a**), 8.25×10^{-5} M (**3c**, **4b**, **5b**), 5.50×10^{-5} M (**3b**, **3g**, **6**), 3.30×10^{-4} M (**4a**), 2.75×10^{-5} M (**3h**), and 2.06×10^{-5} M (**3i**). The solution of model compound and ZnCl₂

was prepared with various molar ratios of ZnCl₂ to the model compound (from 0 to 300), meanwhile the concentration of the model compound was kept always constant. The UV–vis experiments of all samples were made at 25 °C. The difference in absorbance (ΔA) of the model compound in the presence of Zn²⁺ ion and absorbance of Zn²⁺ ion at about 280 nm was recorded and the data were plotted against the concentration of ZnCl₂. The association constant K_a was obtained by using the linear curve fitting based on the Benesi–Hildebrand equation:

$$\frac{1}{A - A_0} = \frac{1}{(\epsilon_c - \epsilon_0)[N]_0} + \frac{1}{(\epsilon_c - \epsilon_0)[N]_0 K_a} \frac{1}{[ZnCl_2]^n}$$

where A is the absorbance of mixture, A_0 is the absorbance of pure model compound, ϵ_c is the molar absorption coefficients of complex, ϵ_0 is the molar absorption coefficients of model compound, $[N]_0$ is the initial concentration of model compound, K_a is the association constant, $[ZnCl_2]$ is the concentration of ZnCl₂, and n is the stoichiometric ratio (ZnCl₂: model compound).

A plot of $(A - A_0)^{-1}$ versus $[ZnCl_2]^n$ should produce a straight line for the correct stoichiometry (n). The association constant was estimated from the slope and intercept of the BH plot. So this titration experiment can provide us both association constant and stoichiometry.

Measurement of Water Sessile Drop Contact Angle

Eighty microliter of solution (3 mg/mL of model compounds in THF) was spin-coated onto a glass slide at 6000 rpm for 2 min (SPINNER SMA AC 6000 from SMA Suministro de Materiales y Asistencia). The water contact angles of samples were measured at 25 °C by injecting a 10 μ L liquid drop (Measuring System DSA 100 from KRÜSS Company). The values are the result of five different measurements discarding the two extreme values and averaging the rest (deviation $\pm 3^\circ$).

RESULTS AND DISCUSSION

Synthesis of Various Model Compounds

Various benzoxazine monomers were conveniently prepared according to the well-established conventional methods: solventless method³⁰ and solution method^{11,31,32} (**1**, Scheme 1). Following our previously reported experimental conditions, six polybenzoxazines have been prepared (**2**, Scheme 1).¹⁵ As for the synthesis of symmetric benzoxazine “dimers” (**3** and **4**, Scheme 1), depending on different substituents three methods²² were adapted: benzoxazine condensation,²⁰ Mannich reaction method,¹⁴ and multistep condensation method²² (Scheme 2). It should be mentioned that although the synthesis of *N*-phenyl “dimer” **3g** was described in a previous report by using method A, the purification was quite difficult.²⁴ Using method B, the

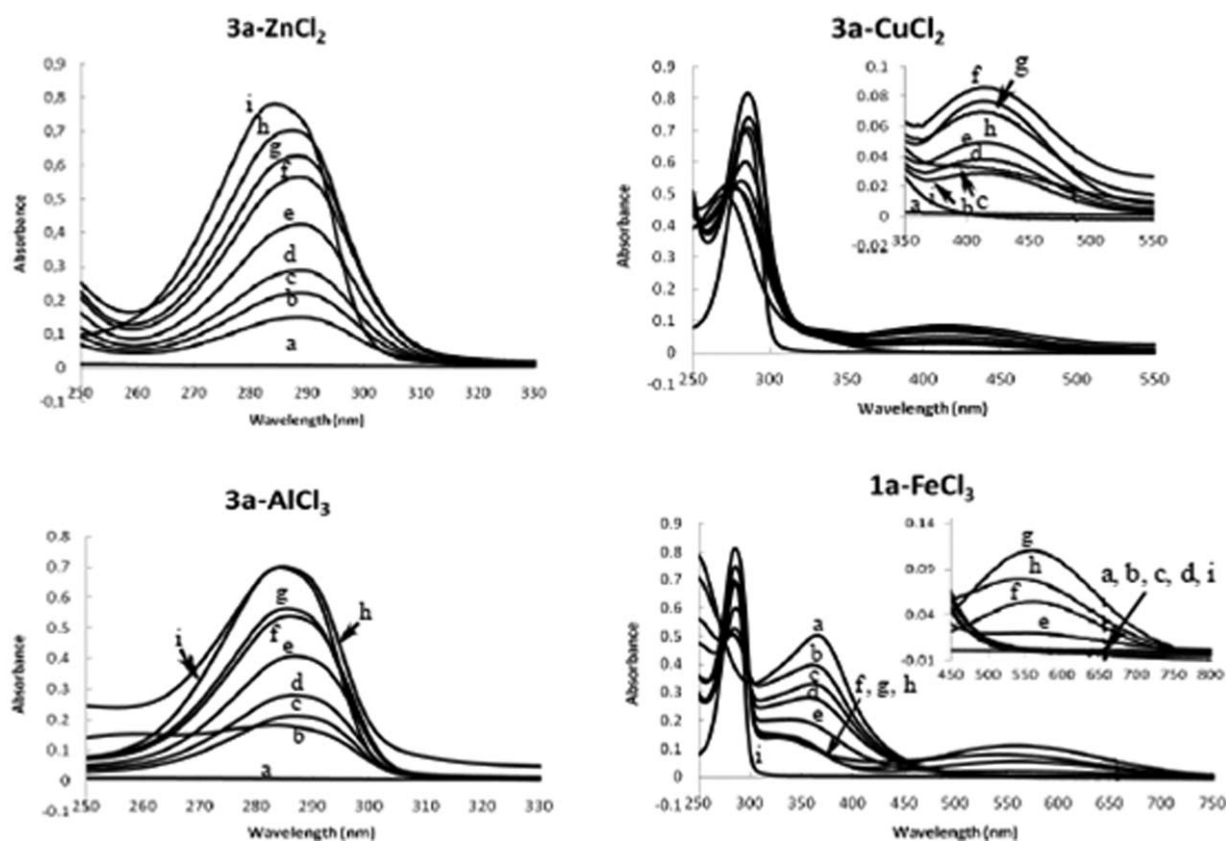


Figure 1. UV-vis spectra of **3a** with different metal ions in methanol at various volumetric ratios (**3a**: metal chloride); (a) 0: 12, (b) 2: 10, (c) 3: 9, (d) 4: 8, (e) 6: 6, (f) 8: 4, (g) 9: 3, (h) 10: 2, and (i) 12: 0.

reaction only provided the corresponding benzoxazine monomer **1f**. Finally, “dimer” **3g** was obtained in good yield by method C. The asymmetric benzoxazine “dimers” and “tetramer” were synthesized by following the reports of Ishida group (**4** and **6**, respectively, Scheme 1).^{24,25,27,28} In the case of “trimers” (**5**, Scheme 1), Ishida and coworkers reported the synthesis of some similar “trimers” with the ortho-positions of the phenolic rings blocked.^{27,28,33} However, in our case, having the ortho-position free, we then adapted an improved multistep condensation method to prepare them. By using dibromide **8**²⁶ instead of the corresponding diol, the “trimers” were obtained in good yields (Scheme 3).

UV-Vis and NMR Studies on the Interaction of a Model Compound with Various Metal Ions

With these model compounds in hand, we firstly investigated the coordination phenomena of symmetric “dimer” **3a** with various metal ions such as Zn^{2+} , Cu^{2+} , Al^{3+} , and Fe^{3+} by UV-vis and $^1\text{H-NMR}$ analysis. Figure 1 shows the UV-vis spectra of the methanol solution of **3a** with CuCl_2 , ZnCl_2 , AlCl_3 , and FeCl_3 for various substrate:metal ratios (from 0:12 to 12:0). Compound **3a** shows a maximum peak at 284 nm. When ZnCl_2 was added, the absorbance of the maximum peak shifts to the red by 5 nm. A new peak at 413 nm appeared when **3a** was mixed with CuCl_2 . These phenomena are in agreement with what is reported in the literature.⁷ In the case of AlCl_3 , similar peak shift was observed (from 284 to 287 nm). A new peak

appeared at 560 nm when FeCl_3 was added. The new peaks at 413 in the case of CuCl_2 , and at 560 in the case of FeCl_3 are not present in the spectra of pure CuCl_2 and pure FeCl_3 . All these results suggest that coordination compounds were formed between the benzoxazine dimer and metal ions.

The interactions of two other dimers, **3c** and **3e**, containing an electron-withdrawing and electron-donor group respectively, with metals were also studied by UV-vis spectroscopy. In all cases clear changes in the absorption bands were also observed (see Supporting Information).

$^1\text{H-NMR}$ analysis was then used to study the coordination complexes and the effect of different metal ions. As shown in Figure 2, when metal ions were added into the $\text{CH}_3\text{OH-d}_4$ solution of symmetric “dimer” **3a**, the peak due to the CH_2 group significantly shifted downfield and splitted, implying the formation of new “dimer”-metal complexes. This behavior was probably due to the reduction of the electron density of the methylene group as a result of the coordination of metal ions with the “dimer” through the aza and methylene group. When Cu^{2+} was added, the peak changed into two broad peaks. For Al^{3+} , the peak splitted clearly into a group of AB systems, and in the case of Zn^{2+} , only one broad peak was observed. All these outcomes reveal that the rigidity of the resulting complexes should be in the order of $\text{Al}^{3+} > \text{Cu}^{2+} > \text{Zn}^{2+}$. It was also found that the other benzoxazine “dimers” gave similar results. Similar studies

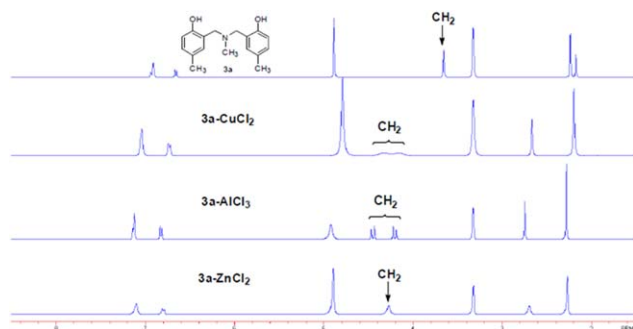


Figure 2. $^1\text{H-NMR}$ spectra of **3a**, **3a-CuCl₂**, **3a-AlCl₃**, and **3a-ZnCl₂** in $\text{CH}_3\text{OH-d}_4$ with a 1:1 ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were also performed with some “dimers,” **3a**, **3b**, **3c**, **3e**, and **3g**, being observed also that CH_2 groups significantly shifted downfield, indicating the formation of complexes (see Supporting Information).

Association Constant Estimation of Model Compound– ZnCl_2 Complexes

To more accurately estimate the efficiency of the metal ion interaction with the model compounds, Zn was selected for a quantitative study. The association constants (K_a) and the stoichiometric ratios for benzoxazine model compound– ZnCl_2 complexes were calculated from Benesi–Hildebrand plots using the UV–vis titration method,³⁴ and the results are listed in Table I. To explain the experimental facts, we will discuss in the following paragraphs, we have proposed some possible structures of various model molecule– ZnCl_2 complexes outlined in Figure 3.

As described in Table I, the stoichiometric ratio of symmetric “dimers” to ZnCl_2 is typically 1:2. The association constant of symmetric “dimer” **3a** with ZnCl_2 is $5.77 \times 10^3 \text{ M}^{-2}$ (Table I, entry 1). Symmetric *N*-allyl “dimer” **3f** gives similar value (Table I, entry 6). As for the symmetric “dimers” with electron-withdrawing groups, such as CN or NO_2 , the corresponding association constant increases significantly (Table I, entries 2 and 3), whereas that of symmetric “dimer” **3e** with electron-donating methoxyl group was unavailable probably due to the too weak interaction with ZnCl_2 (Table I, entry 5). The major interaction of a symmetric “dimer” with ZnCl_2 probably derives from chelate interaction [Figure 3(A)]. An electron-withdrawing group in the aromatic ring increases the acidity of phenol and would greatly stabilize “dimer”– ZnCl_2 intermolecular bonding, therefore the corresponding association constant should be higher, as observed (Table I, entries 2 and 3). On the contrary, a lower association constant would be expected for symmetric “dimer” with electron-donating groups, as obtained (Table I, entries 1 and 5). A special case was the symmetric “dimer” **3d** with CF_3 group that shows a 1:1 stoichiometry ratio (suggesting the bonding of the Zn^{2+} ion with a single molecule of **3d**)^{8,9} and provides a similar association constant value as that of **3a** (Table I, entries 4 vs 1). The reasons why in this case the stoichiometry is different from the other symmetric dimers would merit a further investigation.

In *N*-phenyl “dimer” **3g**– ZnCl_2 complex, a $\text{O-ZnCl}_2 \cdots \pi$ interaction with phenyl group could exist [Figure 3(B)] and as a result, its association constant should be higher than that of *N*-methyl “dimer” **3a**– ZnCl_2 complex, as observed (Table I, compare entries 7 and 1, respectively).

Interestingly, for mono-methylated “dimer” **3h** the association constant decreases to $4.22 \times 10^3 \text{ M}^{-1}$ with a 1:1 stoichiometry probably due to the coordination site loss (Table I, entry 8 compared to entry 2), whereas dimethylated “dimer” **3i** shows very weak interaction with ZnCl_2 and no association constant was measurable (Table I, entry 9). As expected, the stoichiometric ratio of asymmetric “dimers” (**4a**, **4b**, and **4c**) to ZnCl_2 is 1:1 and the association constant is significantly lower than that of the corresponding symmetric “dimers” (**3a**, **3b**, and **3c**). Also here, an increase of the association constant was observed when the substrate was substituted by electron-withdrawing groups (**4b** and **4c** vs. **4a**) (Table I, compare entries 11 and 12 with 10). The structure of asymmetric complexes seems to be similar to that of symmetric “dimer”– ZnCl_2 complexes [Figure 3(C)]. Due to the lack of a phenolic hydroxyl group, the association constants are lower.

In the case of “trimers” (**5a** and **5b**) and the “tetramer” (**6**), according to the reports of Ishida group,^{27,28} they possess a quite stable close-ring geometry due to the strong intramolecular hydrogen bonding [Figure 3(D,E)]. Hence, Zn^{2+} ions cannot easily reach the coordination centers, neither break the internal hydrogen bonds, giving rise to neglectable association constants (Table I, entries 13, 14, and 15, respectively). The same was observed qualitatively for polymer **2a**. These results confirm the

Table I. Summary of the Association Constants (K_a) of Model Compound– ZnCl_2 Complexes Determined by UV–vis Titration Method

Entries	Model compound	Stoichiometric ratio (model molecule: ZnCl_2)	Association constant (K_a) ^a
1	3a	1:2	$5.7 \times 10^3 \text{ M}^{-2}$
2	3b	1:2	$1.0 \times 10^6 \text{ M}^{-2}$
3	3c	1:2	$2.3 \times 10^4 \text{ M}^{-2}$
4	3d	1:1	$2.0 \times 10^3 \text{ M}^{-1}$
5	3e	— ^b	— ^b
6	3f	1:2	$2.5 \times 10^3 \text{ M}^{-1}$
7	3g	1:2	$4.5 \times 10^4 \text{ M}^{-2}$
8	3h	1:1	$4.2 \times 10^3 \text{ M}^{-1}$
9	3i	— ^b	— ^b
10	4a	1:1	47.8 M^{-1}
11	4b	1:1	$3.9 \times 10^2 \text{ M}^{-1}$
12	4c	1:1	$3.6 \times 10^2 \text{ M}^{-1}$
13	5a	— ^b	— ^b
14	5b	— ^b	— ^b
15	6	— ^b	— ^b

^aThe association constants are typically averages of two experiments at 25 °C.

^bThe constant is too small and beyond the limit of UV–vis titration method.

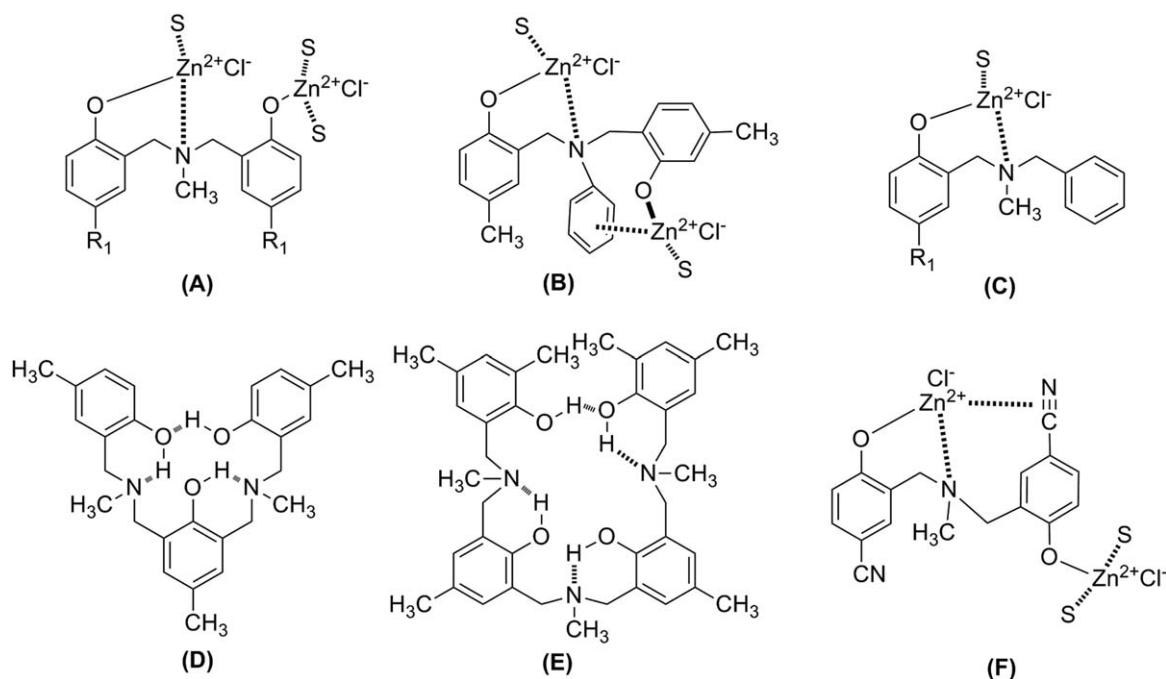


Figure 3. Possible structures of various model molecule–ZnCl₂ complexes (A,B,C,F) and the reported formation of hydrogen bonds in benzoxazine “trimer” and “tetramer” structures (D,E). S = neutral molecules, such as water, methanol or another model molecule.

fact that benzoxazine derived polymers have a strong inner structure mainly formed by intramolecular hydrogen bonds.^{1,24,27}

It is remarkable that “dimer” **3b** shows the highest association constant although the electron-withdrawing ability of cyano group is lower than that of the nitro group. We propose that the cyano group should provide additional interaction with ZnCl₂ as indicated in Figure 3(F), which obviously would help to improve the association constant. Moreover, we surmise that this additional interaction mainly derives from the intramolecular coordination since in the case of di-methylated “dimer” **3i**, the two phenolic groups are blocked and it seems that no strong quela interaction with the metal through the cyano groups is observed; as a result, the association constant is too small to be measured by the UV–vis titration method (Table I, entry 9). These results show that cyano group can provide additional intramolecular coordination for the quela interaction and greatly improve association constant, but the cyano group itself doesn’t interact significantly with Zn²⁺ ion.

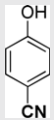
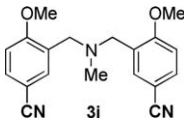
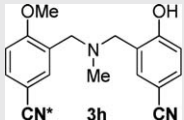
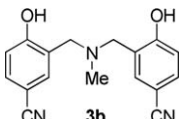
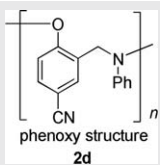
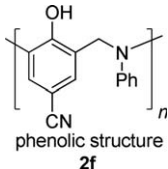
This interpretation is further supported by the following ¹³C-NMR study. As shown in Table II, when ZnCl₂ was added into 4-cyanophenol solution, the peak at 161.66 ppm due to cyano group in the phenolic ring shifted downfield by 0.05 ppm, similarly, as for di-methylated dimer **3i** (Table II, entries 1 and 2). However, in the case of dimer **3b**, the effect was double and the peak shifted by 0.11 ppm (Table II, entry 4). The case of mono methylated “dimer” **3h** is especially interesting. In this case, the cyano group in the phenolic ring exhibited ¹³C chemical shift difference of 0.03 ppm before and after adding ZnCl₂, whereas the cyano group in the anisole ring shifted 0.10 ppm (Table II, entry 3). These outcomes suggest that only one cyano group

coordinates with ZnCl₂ probably as depicted in Figure 3(F), and only the cyano group in the anisole ring of **3h** can coordinate as proposed. A similar behavior was observed for phenoxy polymer **2d** and phenolic polymer **2f** (Table II, entries 5 and 6, respectively). The ¹³C chemical shift difference of cyano group in **2d** before and after adding ZnCl₂ was 0.04 ppm, while in **2f** it was 0.16 ppm. This result is in agreement with what has been discussed if we take into account that in the phenoxy polymer **2d** there are less free phenolic OH groups to form quela interactions, and on the contrary, in the phenolic polymer **2f** many more free phenolic OH groups must exist. The chemical shifts differences described in Table II, being modest, are consistently higher than the ¹³C-NMR digital resolution (0.015 ppm/point), indicating that a correlation exist between the ¹³C-NMR differences (Table II) and the measured association constants (Table I), thus supporting the proposed interpretation (structure F in Figure 3). Moreover, this study indicates that the effects of the cyano substituent in the “dimer” and in the “polymers” are correlated. Therefore, this supports the selection of the “dimer” as model for the “polymers” in the quantitative study, and the fact that the conclusions obtained in the dimer study can be transposed to the polymer.

Water Sessile Drop Contact Angle Study on Various Model Compound Films

To get information about surface energies, and the ability of our model compounds to interact with the surroundings (data of interest when translated to the uses of polybenzoxazines as adhesives, composite matrixes, etc.), we further investigated the interaction of some model compounds with water. Using spin-coating technique, thin films of different model compounds were produced on glass surfaces and the observed water sessile

Table II. ^{13}C -NMR Chemical Shift Values of Cyano Groups in Various Model Compounds in Deuterated DMSO^{a}

Entry	Model compound	Δ (CN) (ppm)		$\Delta\delta(\text{CN})$ (ppm)
		Before adding ZnCl_2	After adding ZnCl_2	
1		161.66	161.71	0.05
2		160.78	160.84	0.06
3		161.24, 161.13	161.34, 161.16	0.10*, 0.03
4		161.06	161.17	0.11
5 ^b		159.49	159.53	0.04
6 ^b		159.39	159.55	0.16

^a Model compound: $\text{ZnCl}_2 = 1:1$ molar, 20 mg of the model compound was used.

^b A broad signal was observed for cyano groups.

drop contact angles are listed in Table III. Generally, contact angle data are used to estimate the components of surface and interfacial tension.^{35,36} Hydrophobicity of some polybenzoxazine derivatives has been measured using this technique.³⁷ In our case, we could foresee that the more the intramolecular bonding, the bigger the water contact angles. As expected, the water contact angle increased in the case of dimers with electron-withdrawing groups (Table III, entries 3, 4 vs 1; 8 vs 6) since the stronger intramolecular hydrogen bonds should confer more rigidity to the structure, making the coordination centers less available for the external water molecules, thus increasing the interfacial tension.

Compared with symmetric *N*-methyl “dimer” **3a**, the water contact angle of symmetric *N*-phenyl “dimer” **3g** increases significantly (Table III, entries 1 vs 5). This phenomenon could be rationalized by considering the fact that more intramolecular bonding exists in symmetric *N*-phenyl dimer **3g** because the free hydroxyl group could also form the $-\text{OH}\cdots\pi$ intramolecular hydrogen bonding interactions with the *N*-phenyl ring.²⁵ In the case of “trimers,” “tetramers,” and polymers, the water contact angles were expectedly higher due to their strong

intramolecular hydrogen bonding (Table III, entries 9–16). It should be pointed out that polymers mainly with phenoxy structure or phenolic structure were prepared by controlling the curing temperature and reaction time.¹⁵ It is remarkable that

Table III. Water Contact Angle Values on Different Model Molecular Films

Entries	Model molecule	Water contact angle (°)	Entries	Model molecular	Water contact angle (°)
1	3a	51	9	5a	81
2	3b	46	10	6	70
3	3c	77	11	2a	76
4	3d	72	12	2b	62
5	3g	71	13	2c	95
6	4a	46	14	2d	90
7	4b	46	15	2e	107
8	4c	52	16	2f	96

phenoxy polymers **2c** and **2d** afforded lower water contact angles than their corresponding phenolic polymers **2e** and **2f**, respectively, which indicates that phenoxy structure has more available hydrogen bonding sites for water interaction, being the phenolic structure forming more intramolecular hydrogen bonds (Table III, entries 13–16).

Interestingly enough, in several very relevant cases, the “dimer” (**3b**, Table III, entry 2) and the polymers (**2b**, **2d**, and **2f**; Table III, entries 12, 14, and 16, respectively) with cyano groups as substituents, significantly lower values for the water contact angles were observed. This behavior is probably due to the additional intermolecular hydrogen bonding between the cyano group and water. It is worth to notice that the cyano substituted dimer **3b** was the model molecule that showed a higher association constant with ZnCl_2 , and in both cases (water and zinc cations) the effects of the cyano substituent seem to be significantly different from the ones observed with other electron-withdrawing substituents. It seems that the cyano group offers extra coordination centers and this is translated into higher association constants and lower contact angles. With these results we can also conclude that both methodologies, the estimation of association constants of model molecules with metals and the simple study of water sessile drop contact angle measurements on films of model molecules, give consistent information about inner structure of polybenzoxazines and their capacity to interact with the surroundings.

CONCLUSIONS

In summary, the interaction of various polybenzoxazines and polybenzoxazine model compounds with metal ions and water was investigated using UV–vis, ^1H -NMR and ^{13}C -NMR analysis, and contact angle measurements. We succeed in calculating the association constants (K_a) for model molecule– ZnCl_2 complexes by UV–vis titration method. In the common case (complexes with 1:2 stoichiometry), it was found that an electron-withdrawing group can stabilize the complex, resulting in a higher association constant. This result suggests a new approach to improve polybenzoxazines metal adhesion. The highest association constant was observed for the **3b**– ZnCl_2 complex probably due to the fact the cyano group provided an additional intramolecular interaction with Zn^{2+} ion. This interpretation was supported by a ^{13}C -NMR study that also confirmed that “dimers” could be used as models of the “polymers” for quantitative studies about the effect of substituents on the interaction with metal ions. The cyano group also provided additional interactions with water as shown by the results from contact angle measurements.

In general, the results reported in this article are related with the rigidity and the low surface energy of the polymers derived from benzoxazines, due, as previously reported, to a strong intramolecular hydrogen bond net. So, in general, unfunctionalized polybenzoxazines show very weak adhesion with metal surfaces. By introducing appropriate substituents (i.e., cyano group), additional coordination centers are created; the model molecules showing a much higher tendency to positively interact with the surroundings (metal ions or water), this effect is also observed in the corresponding cyano functionalized polymers.

Against simple intuition, contact angle measurements show that polymers with major “phenoxy” structure show a higher surface energy than polymers with major “phenolic” structure. This result strongly support the proposed intramolecular hydrogen bond net in the “phenolic” structures.

Our findings should allow modulating the adhesion and other surface properties of the benzoxazine derived polymers by playing with the properties of the substituents and the structure of the polymer.

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REFERENCES

- (a) In Handbook of Benzoxazine Resins; Ishida, H., Agag, T., Eds.; Elsevier Inc.: Amsterdam, **2011**. (b) Kiskan, B.; Narendra, N.; Yagci, Y. *Polym. Int.* **2011**, *60*, 167.
- (a) Ghosh, N. N.; Kiskan, B.; Yagci, Y. *Prog. Polym. Sci.* **2007**, *32*, 1344. (b) Yagci, Y.; Kiskan, B.; Ghosh, N. N. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 5565. (c) Rimdusit, S.; Tiptipakorn, S.; Jubsilp, C.; Takeichi, T. *React. Funct. Polym.* **2013**, *73*, 369. (d) Demir, K. D.; Kiskan, B.; Aydogan, B.; Yagci, Y. *React. Funct. Polym.* **2013**, *73*, 346.
- Ishida, H.; Allen, D. J. *J. Polym. Sci. Part B: Polym. Phys.* **1996**, *34*, 1019.
- Shen, S. B.; Ishida, H. *Polym. Comput.* **1996**, *17*, 710.
- Ishida, H.; Low, H. Y. *Macromolecules* **1997**, *30*, 1099.
- Ishida, H.; Allen, D. J. *Polymer* **1996**, *37*, 4487.
- (a) Phongtamrug, S.; Pulpoka, B.; Chirachanchai, S. *Supramol. Chem.* **2004**, *16*, 269. (b) Laobuthee, A.; Ishida, H.; Chirachanchai, S. *J. Incl. Phenom. Macrocycl. Chem.* **2003**, *47*, 179.
- (a) Chirachanchai, S.; Laobuthee, S.; Phongtamrug, S.; Siripatanarakit, W.; Ishida, H. *J. Appl. Polym. Sci.* **2000**, *242*, 2561. (b) Phongtamrug, S.; Chirachanchai, S.; Tashiro, K. *Macromol. Symp.* **2006**, *40*. (c) Phongtamrug, S.; Tashiro, K.; Miyata, M.; Chirachanchai, S. *J. Phys. Chem. B* **2006**, *110*, 21365.
- (a) Veranitisagul, C.; Kaewwilai, A.; Sangngern, S.; Wattanathana, W.; Suramitr, S.; Koonsaeng, N.; Laobuthee, A. *Int. J. Mol. Sci.* **2011**, *12*, 4365. (b) Zhu, Y.; Gu, Y. *J. Macromol. Sci. Part B: Phys.* **2011**, *50*, 1130. (c) Lekesiz, T. O.; Hacıoğlu, J. *Polymer* **2014**, *55*, 3533.
- Taskin, O. S.; Kiskan, B.; Aksu, A.; Balkis, N.; Weber, J.; Yagci, Y. *Chem. Eur. J.* **2014**, *20*, 10953.
- Ning, X.; Ishida, H. *J. Polym. Sci.: Polym. Chem.* **1994**, *32*, 1121.
- Andreu, C. R.; Reina, J. R.; Ronda, J. C. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 3353.
- Burke, W. J.; Bishop, J. L.; Mortensen Glennie, E. L.; Bauer, W. N. Jr. *J. Org. Chem.* **1965**, *30*, 3423.

14. Burke, W. J.; Smith, R. P.; Weatherbee, C. *J. Am. Chem. Soc.* **1952**, *74*, 602.
15. (a) Liu, C.; Shen, D.; Sebastián, R. M.; Marquet, J.; Schönfeld, R. *Macromolecules* **2011**, *44*, 4616. (b) Schoenfeld, R.; Kreiling, S.; Liu, C.; Shen, D.; Sebastian, R. M.; Marquet, J. EP 2336221 A1 20110622.
16. Zhang, H.; Lu, Z. *e-Polymers* **2010**, *10*, 1578; <http://www.e-polymers.org>.
17. Proponet, C.; Vebrel, J.; Laude, B.; Guenot, P. *Spectrochim. Acta Part A* **1982**, *38A*, 275.
18. Takeichi, T.; Nakamura, K.; Agag, T.; Muto, H. *Des. Monomers Polym.* **2004**, *7*, 727.
19. Harries, H. J.; Orford, B. F. *Inorg. Chim. Acta* **1983**, *68*, 41.
20. Dunders, J.; Ishida, H. *Spectrochim. Acta* **1995**, *51A*, 855.
21. Chirachanchai, S.; Laobuthee, A.; Phongtamrag, S. *J. Heterocycl. Chem.* **2009**, *46*, 714.
22. Bujnowski, K.; Adamczyk, A.; Synoradzki, L. *Org. Prep. Proced. Int.* **2007**, *39*, 417.
23. Komatsubara, T.; Tonogai, S.; Takahashi, A. *Kagaku to Kogyo* **1987**, *61*, 367.
24. Kim, H.; Ishida, H. *Macromolecules* **2003**, *36*, 8320.
25. Kim, H.; Ishida, H. *J. Phys. Chem. A* **2002**, *106*, 3271.
26. Trost, B. M.; Yeh, V. S. C.; Ito, H.; Bremeyer, N. *Org. Lett.* **2002**, *4*, 2621.
27. Goward, G. R.; Sebastiani, I. S.; Spiess, H. W.; Kim, H.; Ishida, H. *J. Am. Chem. Soc.* **2003**, *125*, 5792.
28. Kim, H.; Ishida, H. *Macromol. Symp.* **2003**, *195*, 123.
29. Abou-Zied, O. K. *Spectrochim. Acta Part A* **2005**, *62*, 245.
30. Ishida, H. U.S. Pat. 5,543,516 (1996).
31. Tarek, A.; Jin, L.; Ishida, H. *Polymer* **2009**, *50*, 5940.
32. Andreu, R.; Ronda, J. C. *Synth. Commun.* **2008**, *38*, 2316.
33. Ishida, H.; Krus, C. M. *Macromolecules* **1998**, *31*, 2409.
34. Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.
35. Good, R. J.; van Oss, C. J. In *Modern Approaches to Wettability: Theory and Applications*; Schrader, M. E., Loeb, G. I., Eds.; Plenum: New York, **1992**; pp 1–27.
36. Drelich, J.; Miller, J. D.; Good, R. J. *J. Colloid Interface Sci.* **1996**, *179*, 37.
37. (a) Wang, C. F.; Wang, T. F.; Liao, C. S.; Kuo, S. W.; Lin, H. C. *J. Phys. Chem. C* **2011**, *115*, 16495. (b) Qu, L.; Xin, Z. *Langmuir* **2011**, *27*, 8365. (c) Kumar, K. S. S.; Nair, S. P. R.; Ninan, K. N.; Kulkarni, A. D.; Wadgaonkar, P. P. *Polym. Adv. Technol.* **2009**, *20*, 1107. (d) Liao, C. S.; Wang, C. F.; Lin, H. C.; Chou, H. Y.; Chang, F. C. *Langmuir* **2009**, *25*, 3359.