Smart Polyacids

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A Borinic Acid Polymer with Fluoride Ion- and Thermo-responsive Properties that are Tunable over a Wide Temperature Range[**]

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Abstract: *A new type of smart borinic acid polymer with luminescence and multiple stimuli-responsive properties is reported. In DMSO with small amounts of water, the homopolymer PBA shows a tunable upper critical solution temperature (UCST). As the amount of water increases from 0 to 2.5 % (v/v), the UCST rises linearly from 20 °C to 100 °C (boiling point of water). Thus, the thermal responsive behavior can be tuned over a wide temperature range. Furthermore, polymer solutions in DMSO show a reversible response to fluoride ions, which can be correlated to the presence of the Lewis acidic borinic acid groups. Upon addition of fluoride, the polymer becomes soluble because the functional R_2BOH groups are converted into ionic $[R_2BF_2]^-$ groups, but turns insoluble again upon addition of H_2O, which reverses this process.*

Stimuli-responsive or "smart" polymers that respond to external signals such as changes in temperature, pH, addition of ions, ionic strength, light, stress, and so on, have attracted considerable research efforts, because of their potential applications in biomedicine, sensors, micromechanical and optical systems, cosmetics, and coatings.[1] Thermo-responsive polymers have received special attention, because temperature changes are easy to realize and control. For instance, poly(*N*-isopropylacrylamide) (PNIPAM),[2] one of the most thoroughly studied systems, shows a lower critical solution temperature (LCST) of about 34 °C in water, while that of oligo(ethylene glycol) is 32 °C,[3] poly(ethylene oxide) 96 °C,[4] and poly(*N*,*N*-dimethylaminoethyl methacrylate) 50 °C.[5] Thermo-responsive polymers with tunable critical transition temperatures remain relatively rare and typically rely on variations in copolymer composition.[6] Homopolymers with continuously tunable thermo-responsive properties over a wide temperature range have to our knowledge not been reported to date.

Various boron motifs have been incorporated into polymeric structures through polycondensation, controlled radical polymerization, and also post-polymerization functionalization.[7] Two classes of boron-functionalized polymers have attracted particular interest: 1) conjugated boron polymers and boron chromophore-decorated polyolefins showing bright colors and tunable emissions have great potential for use in electronics, luminescent materials, chemical sensors and bioimaging;[8] and 2) boronic acid-functionalized polymers are attractive for applications in supramolecular materials chemistry[9] as well as disease diagnosis and therapy owing to their ability to reversibly bind to diols as in sugars or RNA.[10]

When boronic acids are incorporated into block copolymers with poly(acrylamide)s, such as PNIPAM, multi-responsive self-assemblies are generated, which in turn respond to pH, temperature, and added sugars or other polyols.[11] Related polymers with more Lewis acidic boroxole functional groups have gained recent attention because they strongly bind to polyols even under biological conditions (neutral pH).[12] However, compared to the extensive studies on boronic acid polymers, borinic acids have received little attention, despite their easy synthesis, high stability, enhanced Lewis acidity, and excellent substrate binding characteristics.[13] Herein, we describe the synthesis of the first example of a well-defined borinic acid polymer that exhibits strong luminescence, an upper critical solution temperature (UCST) in DMSO that is tunable over a wide temperature range, and a reversible response to the presence of fluoride anions.

With a general structure of RR′B−OH, borinic acids typically behave as weak acids; in anhydrous organic solvents they tend to establish an equilibrium with the corresponding anhydride RR′B−O−BRR′, and in some cases oligomeric structures $\{RR'B{-}OH\}_n$ have been observed as a result of Lewis acid–base interactions.[13,14] The properties of borinic acids can be readily fine-tuned by variation of the substituents R and R′.[13d] We designed a new borinic acid derivative (BA), which features both a polymerizable styryl and a triisopropylphenyl (Tip) group. The bulky Tip substituent was chosen to prevent the formation of cross-links owing to dehydration or Lewis acid-based interactions. The monomer BA was obtained with high purity by Stille coupling of *p*-trimethylstannylstyrene and iodophenyl(triisopropylphenyl)borinic acid (**2**) in 81 % yield (Scheme 1). The successful synthesis was confirmed by ^1H NMR analysis (Supporting Information, Figure S3), which shows the presence of the vinyl group in the region from 5.2 to 7.0 ppm and the OH group at 5.82 ppm. The signal of the methyl groups in *ortho*-position to B at 1.21 ppm is broadened owing to hindered rotation. The corresponding ^{11}B NMR spectrum shows a broad peak at 49 ppm, consistent with the tricoordinate borane structure.

RAFT polymerization of BA in THF at 80 °C using azobisisobutyronitrile (AIBN) as the initiator and 2-(dode-

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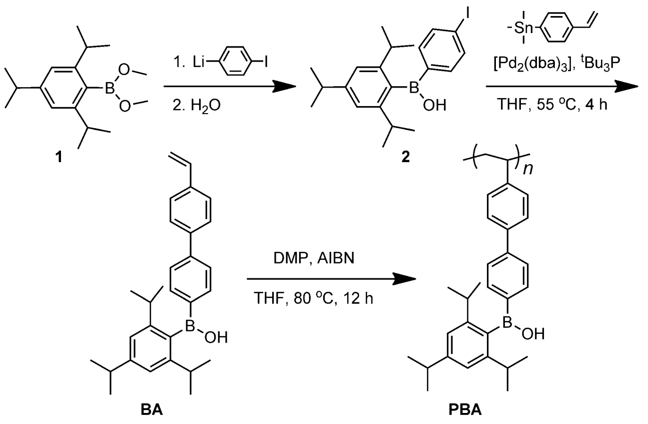

Scheme 1. Synthesis of the borinic acid monomer and corresponding homopolymer. DMP = 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid, dba = dibenzylideneacetone.

cylthiocarbonothioylthio)-2-methylpropionic acid (DMP) as the chain-transfer agent gave the corresponding polymer, PBA, in good yield (Scheme 1). The ^{1}H NMR spectrum of PBA is compared to that of the monomer in the Supporting Information, Figure S3. The borinic acid moiety shows a broad signal at essentially the same chemical shift as the monomer. Based on the integral ratio between the B–OH signal at 5.8 ppm and the C–H proton adjacent to the trithiocarbonate at 4.4 ppm, the degree of polymerization can be estimated to $X_{n,\mathrm{NMR}} = 86$. The ^{11}B NMR signal of PBA experiences a slight upfield shift to 43 ppm relative to the monomer (Supporting Information, Figure S4), which is most likely due to neighboring group effects in the polymer chain. A monomodal symmetric GPC curve indicates that the polymerization is well controlled (Supporting Information, Figure S6).[15] The degree of polymerization $X_{n,\mathrm{GPC}} = 94$ ($Đ = 1.26$) is consistent with the NMR result.

A valuable property of the PBA polymer lies in its strong luminescence under UV irradiation. The monomer BA shows absorption and emission maxima at 294 and 345 nm, respectively, with a high quantum yield of $\Phi_F = 0.82$ in THF (Figure 1, Table 1). In comparison, the absorption band for PBA is slightly blue-shifted to 283 nm, because the π-system of the individual chromophores becomes smaller upon polymerization of the vinyl group. The emission of PBA is similar to that of the monomer, but the band is somewhat broadened and the quantum yield is reduced to $\Phi_F \approx 0.37$, which is possibly due to bimolecular quenching of boron chromophores in the polymer chain.

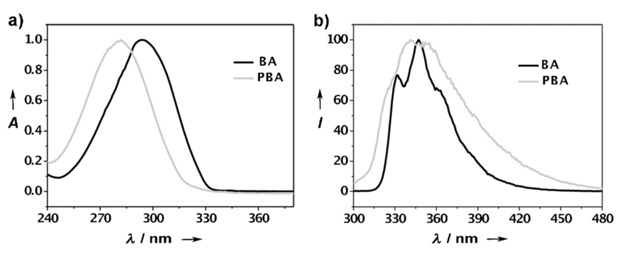

Figure 1. a) Absorption and b) emission spectra of BA and PBA.

Table 1: Photophysical data for BA and PBA in THF.

Sample	λ_{abs} [nm]	ε [L mol^{-1} cm^{-1}]	λ_{em} [nm][b]	Φ_F
BA	294	26300	345	0.82
PBA	283	28100[a]	ca. 330–360	0.37

[a] The molar extinction coefficient of PBA is given per BA repeating unit. [b] All of the samples were excited at the corresponding absorption maximum λ_{abs}.

Another intriguing aspect of the PBA polymer relates to the strong tendency of borinic acid groups to reversibly associate with hydrogen bond donors and acceptors. The role of H-bonding interactions in the self-assembly of molecular borinic acids into larger aggregates has been investigated in detail by X-ray crystallography and NMR spectroscopy.[13b,c,f] The importance of interactions with solvents that can act as H-bonding acceptors or donors (for example, H_2O, MeOH, DMSO, THF) is also well-established.[13c] We decided to carry out further studies on the thermo-responsive properties of PBA in DMSO as the solvent. We discovered that PBA exhibits a tunable and reversible UCST in DMSO in the presence of different amounts of water. As seen in Figure 2a, PBA is not soluble in DMSO below a critical temperature of 22 °C. The solution is opalescent and fluorescent, with a transmittance of less than 10%. As the temperature increases, the PBA solution becomes more and more transparent, with an increase of transmittance from less than 10% to about 100%. Interestingly, we found that the UCST of the PBA solution in DMSO dramatically increases with the amount of water present in solution (Figure 2b). By varying the amount of water from 0 to 2.6%, the UCST can be tuned from 20 °C all the way to 100 °C (boiling point of water). The UCST rises

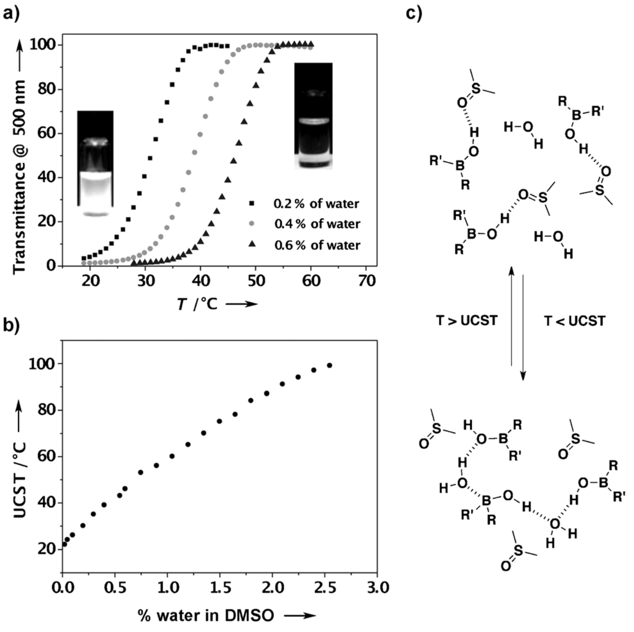

Figure 2. a,b) Plots illustrating the temperature-responsive properties of PBA in DMSO (1 mg mL^{-1}) in the presence of different amounts of water (v/v) ([PBA] = 1 mg mL^{-1}). The temperature with a transmittance of 50% is used to determine the UCST. c) Illustration of the proposed mechanism.

almost linearly with the amount of added water, which suggests potential utility in trace water detection.[16]

The dramatic change in UCST with a very small change in the amount of water present (that is, a small change of solvent polarity) indicates that not only hydrophobic effects but also H-bonding is likely to play an important role. In copolymers with tunable UCST, the ratio of H-bonding polar comonomer to hydrophobic comonomer generally determines the UCST.[6] The homopolymer PBA contains H-bonding B-OH moieties as well as the hydrophobic Tip pendent groups and polymer backbone. In DMSO, the polymer solution is stabilized in part by H-bonding interactions with the solvent (a crystal structure of compound **2** reveals H-bonding to DMSO solvent, but full refinement was not possible). Upon addition of water, these H-bonding interactions become less favorable than the polymer–polymer interactions, resulting in polymer precipitation, possibly because water molecules displace the DMSO and bridge different polymer strands as illustrated in Figure 2c.[17] The PBA solution turns homogeneous once again when the temperature is higher than the UCST, where the polymer–solvent(DMSO) interaction is more favorable than the polymer–polymer interaction.

Another interesting aspect is that, owing to the presence of the empty p orbital, tricoordinate organoboranes are known to accommodate a lone pair of electrons from a Lewis base, resulting in often very high affinity for anions and other neutral bases.[8d,18] In the case of organoboranes with π-conjugated substituents, formation of the Lewis acid–base complex typically results in a distinct change in the absorption and emission characteristics.[19] As a consequence, organoboranes show superior performance as chemical sensors, for example, for fluoride and cyanide anions.

We decided to investigate the response of the luminescent borinic acid polymer PBA to fluoride anions. The initial PBA solution in DMSO with 0.9% of water is opalescent, while upon addition of 10 equiv of tetrabutylammonium fluoride (TBAF) the solution becomes transparent (Figure 3a). This process is reversed by addition of 6 equiv of water, and all these changes are readily detected by naked eye. To quantify the turbidity changes, transmittance measurements were carried out by UV/Vis spectroscopy and particle sizes were determined by dynamic light scattering (DLS). Prior to the addition of TBAF, the transmittance of the solution is only about 20%, which is due to the presence of PBA particles with an average diameter of 531 nm (Figure 3b,c). With increasing amounts of TBAF in the solution, the transmittance is enhanced (56% at 1, 84% at 2, and 100% at 10 equiv of added TBAF) and the average particle size decreases to 255 nm with 1, 32 nm with 6, and 6.5 nm with 10 equiv of TBAF. We attribute this phenomenon to the increased solubility of the polymer upon binding of fluoride anions to the borane moieties. The PBA solution in DMSO with 10 equiv of TBAF is perfectly transparent, as the polymer is molecularly dissolved. However, upon addition of water the transmittance decreases once again and the solution becomes turbid (Figure 3d).

To better understand the origin of the observed response of the polymer to fluoride ions, corresponding experiments were performed on the precursor molecule **2** as a molecular model system. The aromatic region of the ^{1}H NMR spectrum of **2** in [D$_6$]DMSO shows signals for the phenyl protons at 7.8 ppm and 7.4 ppm, while the protons for the Tip group appear at 7.0 ppm (Figure 4a). Upon addition of 1.0 equiv of TBAF, new signals appear at 7.3, 7.1, and 6.7 ppm, indicating that a different species had formed (Figure 4b). Quantitative conversion to this new species is reached at about 2.2 equiv of added TBAF (Figure 4c). At the same time, the ^{11}B NMR signal at 52.4 ppm is displaced by a new sharper signal in the region typical of tetracoordinate boron at 11.1 ppm, and a new peak also emerges at −129 ppm in the ^{19}F NMR spectrum (Supporting Information, Figure S7). All the data are consistent with formation of a difluoroborate complex Tip-BF$_2$-PhI (**3**), which was further confirmed by matrix-assisted laser desorption ionization mass spectrometry

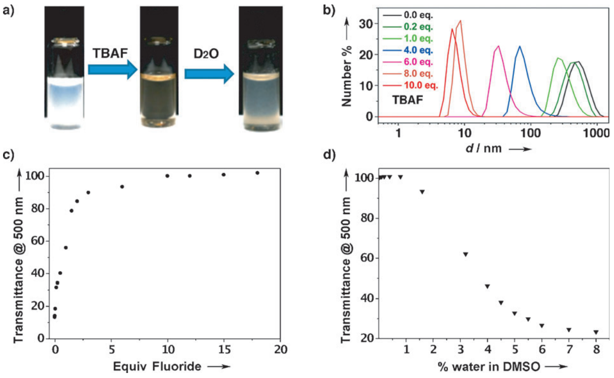

Figure 3. Illustration of the fluoride ion-responsive properties of PBA in DMSO (1 mg mL^{-1}). a) Photographs of a PBA solution in DMSO containing 0.9% water, upon addition of 10 equiv of TBAF and then 8% water. b) Particle size distributions for PBA solutions in DMSO/0.9% water upon addition of different amounts of TBAF. c) Transmittance of a PBA solution in DMSO/0.9% water upon addition of different amounts of TBAF. d) Transmittance of a PBA solution with 10 equiv of TBAF in DMSO upon addition of different amounts of water.

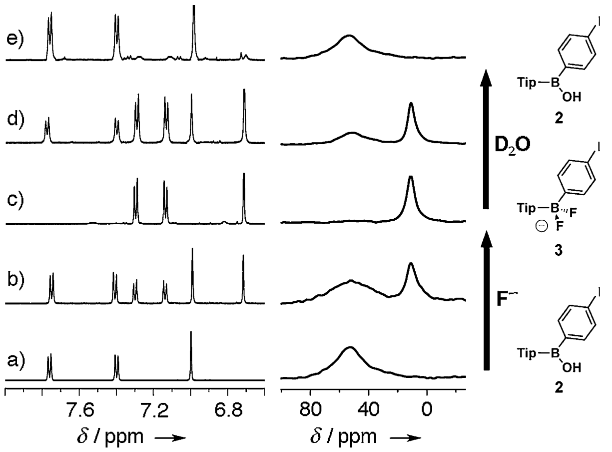

Figure 4. a) ^{1}H (aromatic region) and ^{11}B NMR spectra of compound **2** in [D$_6$]DMSO. b) After addition of 1.0 equiv of TBAF. c) After addition of 5.0 equiv of TBAF. d) Followed by addition of 16 µL (3.2%) of D$_2$O. e) Followed by addition of 48 µL (9.6%) of D$_2$O. Right: corresponding molecular structures.

(MALDI-MS, negative mode). Upon addition of an excess of deuterated water, the borinic acid **2** is regenerated (Figure 4 d,e). The reversal of the fluoride binding process in the presence of water is attributed to the high hydration enthalpy of fluoride ions.[18a] Importantly, the results are consistent with our observations for the polymer, PBA, where initial fluoride anion binding results in formation of a fluoroborate polyelectrolyte that is well-soluble in DMSO, while addition of water regenerates the neutral PBA polymer, which then phase-separates from the solvent.

In conclusion, we report the first example of a well-defined borinic acid polymer with strong luminescence, high stability, and multiple stimuli-responsive properties. In DMSO solution, the homopolymer shows a linear relationship between the UCST (20 °C to 100 °C) and the amount of added water (0 to 2.5 % (v/v)), indicating potential use in trace water detection and release applications. The borinic acid polymer binds fluoride ions in DMSO, resulting in formation of a charged fluoroborate polyelectrolyte. This process can be reversed by simple addition of small amounts of water. The borinic acid polymer introduced in here thus represents a new type of stimuli-responsive polymer that holds great potential as a smart material and in detection and diagnostics applications.

Experimental Section

Borinic acid monomer (BA): A catalyst solution consisting of [Pd$_2$(dba)$_3$] (148 mg, 0.16 mmol) and tBu$_3$P (260 mg, 1.29 mmol) in THF (10 mL) was added to a Schlenk tube containing a solution of borane **2** (2.00 g, 4.61 mmol) and 4-trimethylstannyl styrene (2.58 g, 9.66 mmol) in THF (10 mL). The mixture was heated to 55 °C for 4 h. After workup with CH$_2$Cl$_2$/water, the crude product was subjected to column chromatography on silica gel with hexanes/CH$_2$Cl$_2$ mixture as the eluent. Precipitation into hexanes and drying in high vacuum gave the product as a white powder. Yield: 1.54 g (81 %). ^{1}H NMR (499.895 MHz, CDCl$_3$): $\delta = 7.89$ (d, $^3J = 8.0$ Hz, 2 H, Ph), 7.64 (overlap, 4 H, Ph), 7.51 (d, $^3J = 8.5$ Hz, 2 H, Ph), 7.07 (s, 2 H, Tip), 6.78 (dd, $^3J = 17.5$ and 11.0 Hz, 1 H, Vi), 5.82 (d, $^3J = 18.0$ Hz, 1 H, Vi), 5.82 (s, 1 H, B-OH), 5.30 (d, $^3J = 11.0$ Hz, 1 H, Vi), 2.96 (septet, $^3J = 8.0$ Hz, 1 H, iPr), 2.73 (septet, $^3J = 8.0$ Hz, 2 H, iPr), 1.33 (d, $^3J = 7.0$ Hz, 6 H, iPr), 1.21 ppm (broad, 12 H, iPr). ^{11}B NMR (160.386 MHz, CDCl$_3$): $\delta = 49$ ppm ($w_{1/2} = 1500$ Hz). ^{13}C NMR (125.698 MHz, CDCl$_3$): $\delta =$ 150.8, 149.7, 144.0, 140.5, 137.2, 136.6, 136.2, 127.5, 126.9, 126.5, 120.6, 114.3, 35.1, 34.6, 24.9 (broad), 24.3 ppm. High-resolution MALDI-MS: $m/z = 819.5805$ $[M_2-\mathrm{H}]^-$ (100 %, calcd for C$_{29}$H$_{35}$BO)$_2$ 819.5496; 409.2702 $[M-\mathrm{H}]^-$ (20 %, calcd for C$_{29}$H$_{34}$BO 409.2702.

Homopolymer (PBA): BA monomer (410 mg, 1.00 mmol), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DMP)[20] (3.6 mg, 10 μmol), AIBN (0.2 mg, 1.0 μmol), and THF (0.5 mL) ([BA]/[DMP]/[AIBN] = 100:1:0.1) were loaded into a Schlenk tube. After 3 freeze–pump–thaw cycles, the tube was immersed in an 80 °C oil bath and kept stirring for 12 h. The reaction was terminated by placing the tube in liquid nitrogen. The polymer was then precipitated into a 10-fold volume of methanol/H$_2$O (5:1). After drying in high vacuum, the polymer PBA was obtained as a light yellow powder. Yield: 317 mg (77 %). GPC-RI: M$_n$, GPC-RI = 38.5 kg mol^{-1}, $Đ = 1.26$, $X_{n,\mathrm{GPC}} = 94$. ^{1}H NMR (499.895 MHz, CDCl$_3$): $\delta = 8.0$–7.6 (2 H, Ph), 7.6–7.0 (4 H, Ph/Tip), 7.0–6.9 (2 H, Ph), 6.9–6.1 (2 H, Ph), 5.9–5.6 (1 H, B-OH), 3.0–2.8 (1 H, iPr), 2.8–2.6 (2 H, iPr), 2.1–0.8 (3 H, backbone), 1.4–1.2 (6 H, iPr), 1.2–0.9 ppm (12 H, iPr). ^{11}B NMR (160.386 MHz, CDCl$_3$): $\delta = 42.0$ ppm ($w_{1/2} = 2700$ Hz). ^{13}C NMR (125.698 MHz, CDCl$_3$): $\delta = 150.6$, 149.5, 145.5 (broad), 144.0, 138.4, 136.5, 129.5–126.4 (overlap), 126.5, 126.4–125.3 (overlap), 120.8, 34.5, 30.7, 24.5, 22.6 ppm.

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[16] FT-IR measurements and Karl-Fischer titrations are more sensitive and allow for water detection in the ppm level range (S. K. Macleod, *Anal. Chem.* **1991**, *63*, 557–566), whereas our method is operationally simpler and suitable for higher levels of H_2O.

[17] For precedents of water-bridged structures of molecular borinic acids, see ref. [13a]. Water molecules could in principle also form Lewis acid-base complexes with the borinic acid moieties, but the ^{11}B NMR signal of **PBA** in [D$_6$]DMSO remained unchanged in the presence of small amounts of water even at low temperature ($T = 193$ K). Similarly, direct association of borinic acid moieties is unlikely given the presence of the bulky Tip groups.

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