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Nitrocatecholic Copolymers – Synthesis and their Remarkable Binding Affinity†

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Nitrocatecholic random copolymers were obtained from nitration of protected catechol-*N*-isopropylacrylamide copolymers. Incorporation of 5% nitrocatecholic counits can lead to remarkable enhancement of binding affinity toward Fe_3O_4 nanoparticles and an organic boronic acid by a factor of 40 and 20, respectively.

Catechol derivatives have been demonstrated as versatile agents for widespread applications in systems involving interface interactions due to their high binding affinity with both organic and inorganic materials. Various catecholic polymers have been developed for adhesion to a wide range of materials for applications in fields including cell visualization, bacterial sequestration, environmental remediation, stabilization of nanoparticle systems (e.g. Fe_3O_4), dentistry and drug delivery.[1] In this paper, we report the synthesis of structurally well-defined *nitrated* catecholic copolymer and the remarkable enhancement in the binding affinity toward Fe_3O_4 nanomagnate and boronic acids due to the introduction of nitro group. Our new nitrated copolymer system can be applied to systems extensively investigated using numerous catechol derivatives.[1j] In addition, nitration can reduce the tendency of catechol oxidation and lower the undesired aggregation of iron oxide *NPs* and instability of catechol boronate.[1i, 2] For instance, ultrastable iron oxide *NPs* were reported from copolymers carrying just one nitrocatechol chain end group.[2c, 3]

Poly(*N*-isopropylacrylamide) (PNIPAM) is one of the most extensively investigated thermo-responsive polymers with a lower critical solution temperature (LCST) at 32 °C,[4] ideal for drug delivery and bio-separation.[5] PNIPAM with nitrocatechol chain end groups was coated onto iron oxide *NPs* to prepare thermo- and magneto-responsive core-shell *NPs*,[6] facilitating reversible phase transformation without detachment of the anchored PNIPAM chain.[7]

PNIPAM-nitrocatecholic random copolymers carrying multiple multidentates can potentially show improved binding affinity toward various surfaces,[8] e. g. iron oxide *NPs*, and prevent the loss of loaded bortezomib and other boronic bioactive molecules in biomedical applications. However, the coating of iron oxide *NPs* using random nitrocatecholic copolymer with random counit distribution has not been reported. This may be partially due to the challenges of obtaining such polymers. The complications involved in random nitrocatecholic copolymer synthesis including inhibition and chain transfer from nitrocatechol in free radical polymerizations[9] and the incomplete graft of nitrocatechol to precursor polymers.[10]

The magnitude of difference in the binding affinity of nitrocatecholic and catecholic polymers, a subject significant concern, has not yet been established. This is potentially important information for the area of adhesion.

We obtained the quantitative enhancement of the polymer binding affinity to Fe_3O_4 *NPs* due to the introduction of nitro group to the catechol functionality through competitive binding studies of the two copolymers to Fe_3O_4 *NPs*. The binding constants of the two copolymers to an organic boronic acid, 4-fluorophenylboronic acid, were measured directly using ^{1}H NMR.

The nitrated random copolymers, poly(6-nitrodopamine methacrylamide-*co*-*N*-isopropylacrylamide) i.e. P(***N***DMA-*co*-NIPAM), were obtained via nitration of the corresponding protected parent polymers synthesized from radical copolymerization of *N*-isopropylacrylamide (NIPAM) and the protected dopamine methacrylamide (DMA),[11] **Scheme 1**. To circumvent the retardation and inhibition side reactions from the catechol, various strategies have been developed, including using alkyl groups, silyl groups and boronate groups to protect catechol monomers.[1j, 12] In this work, *tert*-butyldimethylsilyl (TBDMS) chloride was used as the capping agent to form the protected *N*-(3, 4-bis((*tert*-butyldimethylsilyl)oxy)phenethyl)methacrylamide (***S***DMA). Poly(*O,O'*-bis(*tert*-butyldimethylsilyl)dopamine

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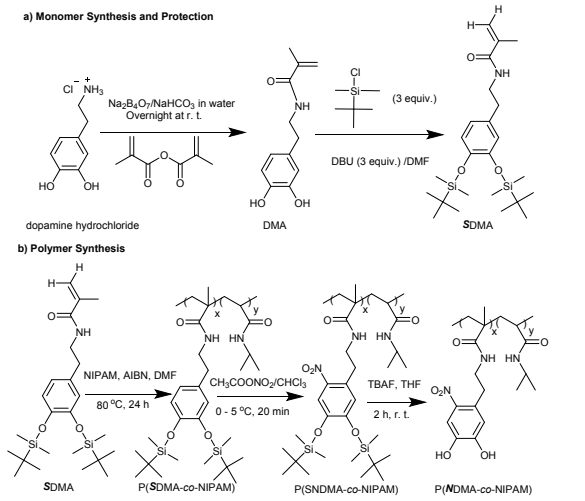

Scheme 1 Poly(6-nitrodopamine methacrylamide-*co*-*N*-isopropylacrylamide) - Synthetic Route.

methacrylamide-*co*-*N*-isopropylacrylamide), P(***S***DMA-*co*-NIPAM) was synthesized through conventional thermal free radical copolymerization. The bulky ***S***DMA comomomer tends to copolymerize with the smaller NIPAM to form random copolymers. The protected copolymer, P(***S***DMA-*co*-NIPAM), was nitrated using fresh acetyl nitrate in chloroform.[13] The TBDMS protected hydroxyl groups, capable of surviving the mild nitration conditions[14] without quinone formation and cross-linking, was then deprotected using tetrabutylammonium fluoride (TBAF)[13] in the presence of an anti-oxidant, ascorbic acid. Poly(dopamine methacrylamide-*co*-*N*-isopropylacrylamide) i.e. P(DMA-*co*-NIPAM), and P(***N***DMA-*co*-NIPAM) were first isolated by precipitation and washed repeatedly using hexane in a Soxhlet apparatus to remove TBDMS. The isolated copolymers were further purified by dissolving in methanol and reprecipitating using HCl (pH=2) six times to remove ascorbic acid, TBAF and other water soluble impurities. The pair of copolymers, P(DMA-*co*-NIPAM) and P(***N***DMA-*co*-NIPAM), were prepared from the same parent polymer, P(***S***DMA-*co*-NIPAM). Thus, P(DMA-*co*-NIPAM) and P(***N***DMA-*co*-NIPAM) involved in the competitive binding experiments differ essentially only by the nitro functionality.

The structures of the monomers and copolymers were established using NMR (Fig. S1-S10, ESI†). Only two aromatic peaks at 7.5 ppm and 6.7 ppm remained in the ^{1}H NMR spectrum of P(***N***DMA-*co*-NIPAM) (Fig. S8, ESI†), indicating a complete nitration of P(***S***DMA-*co*-NIPAM). In the 2D NOESY spectrum of P(***N***DMA-*co*-NIPAM) (Fig. S10, ESI†), the peak at 1.0 ppm assigned to the methyl groups in NIPAM moieties, has NOE cross-peaks with most protons of ***N***DMA moieties, including the aromatic peak at 7.5 ppm and 6.7 ppm, suggesting that the distance between the aromatic protons in ***N***DMA moieties and the methyl groups in NIPAM moieties is less than 5 Å. In contrast to the 2D NOESY of poly(6-nitrodopamine methacrylamide) homopolymer (Fig. S12, ESI†), the absence of aromatic cross peaks in the 2D NOESY of P(***N***DMA-*co*-NIPAM) excludes vicinal ***N***DMA in P(***N***DMA-*co*-NIPAM) copolymers. The copolymers were prepared with two feed mole percent of ***S***DMA (5% and 10%, denoted as polymer-x%, P-x%). The mole ratios of comonomer units in the copolymers were obtained from the ^{1}H NMR (Fig. 2): peak #13, 6.4 ppm of catechol groups, peaks #1, 10.4 ppm and #2, 9.8 ppm of nitrocatechol groups, and peaks #12, 7.2 ppm of amide groups. The copolymer compositions found are close to the feed mole ratios (Table S1, ESI†).

The number average molecular weight ($\overline{M_n}$: 14.5 KDa-17.0 KDa) and the polydispersity indices (PDI: 1.4-1.9) of the copolymers (Table S1, ESI†) were estimated from gel permeation chromatography (GPC), using THF as eluent and linear polystyrene as standards (Fig. S13, ESI†). P(DMA-*co*-NIPAM) and its nitro derivative display similar $\overline{M_n}$. Our $\overline{M_n}$ (15.5 KDa) of P(DMA-*co*-NIPAM)-5% from copolymerization of the protected monomer is much higher than the reported $\overline{M_n}$ (2.1 KDa) of P(DMA-*co*-NIPAM)-5% obtained under similar polymerization conditions from *un*protected comonomers.[15] Our much higher molecular weight by a factor of seven can be attributed to lowering chain transfer during polymerization.

A competitive binding study of P(DMA-*co*-NIPAM) and P(***N***DMA-*co*-NIPAM) to the surface of Fe_3O_4 *NPs* was carried out to establish the quantitative ratio of their binding abilities. The spinel Fe_3O_4 *NPs* with an average diameter of 12-15 nm were confirmed by wide angle X-ray scattering and transmission electron microscopy (TEM) (Fig. 1(a), Fig. S14 and Fig. S15, ESI†). A typical binding study performed in triplicates was carried out as follows: a total of 50 mg of P(DMA-*co*-NIPAM) and P(***N***DMA-*co*-NIPAM) with a targeted mole ratio was dissolved in 5 mL of methanol. Then 5 mL of Fe_3O_4/methanol suspension (~3 mg/mL) was injected into the polymer solution under vigorous agitation by sonication. The experiment of the competitive binding was performed in an ice-water bath under a N_2 atmosphere. The polymer ratio in the reaction solution supernatant was monitored using ^{1}H NMR (Table S2, ESI†). After an equilibrium was established in less than 30 min, the polymer-Fe_3O_4 *NPs* were separated from the reaction mixture using a magnet. The polymer mixture on the surface of Fe_3O_4 *NPs* was recovered by dissolving the Fe_3O_4 *NPs* using concentrated hydrochloric acid in an ice bath for five minutes. To avoid the oxidation of P(DMA-*co*-NIPAM) by ferric cations, ascorbic acid was added during the dissolution of Fe_3O_4 *NPs*. In the absence of ascorbic acid, P(DMA-*co*-NIPAM) could be oxidized by Fe^{3+} and cross-linked.[3] Subsequently, the polymer mixture was purified by dissolving in methanol followed by reprecipitation three times using diluted hydrochloric acid to fully remove iron cations, ascorbic acid and other impurities. After drying in a vacuum, the polymer ratio was determined using ^{1}H NMR. The competitive binding reaction between P(DMA-*co*-NIPAM) and P(***N***DMA-*co*-NIPAM) derived from the same parent P(***S***DMA-*co*-NIPAM) on the same Fe_3O_4 *NPs* under the same conditions leads to rigorous determination of factor of binding enhancement due to the introduction of nitro group, i.e. Enhancement Factor (EnF).

The characterization of the materials after binding Fe_3O_4 and boronic acid was carried out by methods including TEM

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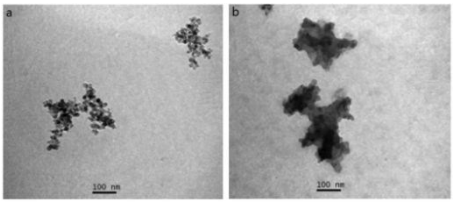

Fig. 1 TEM images of copolymers coated Fe_3O_4 *NPs* before (**a**) and after (**b**) staining using PTA. The molar ratio of P(***N***DMA-*co*-NIPAM)-5% to P(DMA-*co*-NIPAM)-5% on the surface of *NPs* is about 2.8 obtained from ^{1}H NMR of polymer mixture removed from *NPs* surface.

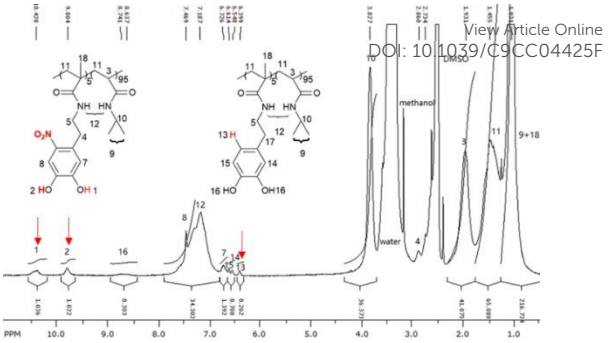

Fig. 2 ^{1}H NMR spectrum of a polymer mixture separated from polymer-Fe_3O_4 *NPs*.

(Fig. 1(a) and 1(b)), NMR (Fig 2, Fig. S20-S23, Table 1, Table S2), FT-IR (Fig. S16-S19) and thermogravimetric analysis (TGA) (Table S3). As shown in the TEM images of polymer-5%-Fe_3O_4 *NPs* (Fig. 1), phosphotungstic acid (PTA) stained *NPs* (Fig.1(b)) show similar size of clusters with the *NPs* before staining (Fig.1(a)), but with polymer stained coating clearly visible.[16]

The composition of the coated *NPs* was also conducted by TGA, showing about 10 % of weight polymer coating for all of the polymer-Fe_3O_4 *NPs* (Table S3, ESI†).

FT-IR was applied to establish the modes of polymer-nanoparticle interactions. First, it was established that PNIPAM does not bind to Fe_3O_4 NPs. No evidence of PNIPAM bound to Fe_3O_4 *NPs* was found, from the IR spectrum of naked Fe_3O_4 *NPs* (15 mg) sonicated with PNIPAM (50 mg) in 10 mL of methanol in an ice-water bath for 30 minutes, followed by rinsing thoroughly using methanol under sonication (Fig. S16, ESI†). For the polymer-*NPs*, C-O-Fe vibration bands of P(DMA-*co*-NIPAM) and P(***N***DMA-*co*-NIPAM) show the expected bathochromic shift after polymer-Fe_3O_4 *NPs* formation. The C-O stretching vibrations shift from 1280 cm^{-1} to 1256 cm^{-1} for P(DMA-*co*-NIPAM) and from 1286 cm^{-1} to 1275 cm^{-1} for P(***N***DMA-*co*-NIPAM) (Fig. S17-S19, ESI†). For P(***N***DMA-*co*-NIPAM), the symmetric NO_2 vibration shifts to 1325 cm^{-1} from 1331 cm^{-1} after binding to Fe_3O_4 *NPs* (Fig. S18-S19, ESI†).[2c] Additionally, the IR spectra of the two polymer-*NPs* systems display characteristic peaks of PNIPAM segments unbonded to *NPs* directly (Fig. S16-S19, ESI†).[17]

The binding affinity can be evaluated based on the bound/free polymer ratio. The determination of the Enhancement Factor, EnF, was carried out from the competitive binding of catecholic copolymer and its nitrated derivative to *NPs* based on the ratios of two polymers on the surface of Fe_3O_4 *NPs* ($\frac{[\mathbf{N}\text{DMA - }\mathit{NPs}]}{[\text{DMA - }\mathit{NPs}]}$) and in the supernatant of the reaction solution ($\frac{[\mathbf{N}\text{DMA}]}{[\text{DMA}]}$) at equilibrium, Equation (1):

$$\mathbf{EnF} = \frac{[\mathbf{N}\text{DMA - }\mathit{NPs}]}{[\text{DMA - }\mathit{NPs}]} \Big/ \frac{[\mathbf{N}\text{DMA}]}{[\text{DMA}]} \quad (1)$$

Quantitative data were from ^{1}H NMR peak intensity. The well-resolved hydroxyl proton signals from P(***N***DMA-*co*-NIPAM) (10.4 ppm and 9.8 ppm) and the aromatic signal (6.4 ppm) from P(DMA-*co*-NIPAM) were selected to evaluate the ratios of polymers (Fig. 2).

The initial and the equilibrium ratios of the two polymers in the two phases for EnF determination were obtained from ^{1}H NMR (Table 1). Three (P-5%) and two (P-10%) starting ratios of polymer compositions were used to determine the EnF. For P-5% copolymer, EnF values higher than 40 were obtained from triplicate experiments, a remarkable enhancement upon introduction of just 5 % the nitro group. For P-10% copolymer, similar levels of EnF indicate that less than 5% of nitro counits are already capable of securely anchoring the copolymer chain to the surface of Fe_3O_4 *NPs*. Thus, the results from the two compostions gave a good overall idea of the system. Homopolymer of NDMA can also be prepared (Fig. S11, ESI†). This observation is consistant with the reported high temperaure stability of binding to Fe_3O_4 *NPs* by poly(ethylene glycol) with a single nitrodopamine end group.[3] In a different approach, the EnF was estimated from the initial weight of each polymer, the total weight loss from TGA and the polymer ratio on the surface of Fe_3O_4 *NPs* from ^{1}H NMR. This approach gives similar values of EnF, (Table S3, ESI†), without involving the polymer ratio in supernatant obtained from ^{1}H NMR.

The binding constants of catechol, 4-nitrocatechol, and the copolymer pair to 4-fluorophenylboronic acid (FPBA) were obtained in PBS solutions at different pH. ^{1}H NMR was utilized in monitor of tetrahedral boronate ester formation till an equilibrium was established (selected ^{1}H NMR spectra are shown in Fig. S20-S23, ESI†). The binding constant of 4-nitrocatechol to FPBA is about 18 times higher than catechol at pH 6.5, and 4-5 times at pH 7.4. The binding affinity levels off at pH 8.5 due to the large increase of catecholate concentration with the rising pH (Table S4, ESI†).

The aqueous soluble P-5% copolymers were selected to

Table 1 The EnF of binding affinity to Fe_3O_4 *NPs* due to nitration of the protected catecholic copolymers[a]

Catechol % in polymer	Starting ***N***DMA/DMA	***N***DMA/DMA in supernatant at equilibrium[b]	***N***DMA-*NPs*/DMA-*NPs* at equilibrium[c]	EnF[d]
5%	0.122	0.067±0.016	2.8±1.5	41.0±1.1
5%	0.213	0.185±0.014	8.0±0.8	43.1±0.3
5%	0.556	0.377±0.036	15.4±3.9	40.5±7.7
10%	0.109	0.073±0.002	3.1±0.5	43.1±7.2
10%	0.189	0.155±0.045	6.6±2.6	41.7±6.7

[a] Standard deviations from triplicate experiments shown. [b] The mole ratio of the two copolymers in methanol supernatant at reaction equilibrium. [c] The mole ratio of the two copolymers on Fe_3O_4 *NPs* at reaction equilibrium. [d] The EnF of P(***N***DMA-*co*-NIPAM) over P(DMA-*co*-NIPAM) obtained, equation (1).

study the influence of the nitro group on the binding affinity to FPBA at pH 6.5 and pH 7.4, exhibiting similar EnF with small molecules. The concentrations of diol moieties in polymer chains were used to calculate binding constants. At pH 7.4 and 20 °C, $K_{P(NDMA\text{-}co\text{-}NIPAM)\text{-}FPBA}$ (2830 M-1) is about 5 times higher than $K_{P(DMA\text{-}co\text{-}NIPAM)\text{-}FPBA}$ (550 M^{-1}). At pH 6.5 and 15 °C below LCST, $K_{P(DMA\text{-}co\text{-}NIPAM)\text{-}FPBA}$ (90 M^{-1}) and $K_{P(\textbf{\textit{N}}DMA\text{-}co\text{-}NIPAM)\text{-}FPBA}$ (2120 M^{-1}) reflect a more than 20 times higher binding ability to FPBA of P(***N***DMA-*co*-NIPAM)-5% (Table S4, ESI†). The lower binding ability of polymers to FPBA, compared to catechol and 4-nitrocatechol, might be due to the steric hindrance and lower accessibility to the diol functionalities.[1i]

In conclusion, we have successfully demonstrated a strategy to prepare nitrocatecholic random copolymers using radical polymerization of vinyl monomer with protected catechol moieties, followed by nitration, thus circumventing the adverse side reactions, including chain transfer, inhibition and crosslink. The enhancement of the binding affinity toward Fe_3O_4 *NPs* due to the incorporation of the nitro group was assessed through competitive binding by two copolymers originating from the same parent copolymer with only the nitro group difference. Upon the introduction of the nitro group to the copolymers, a remarkable enhancement of binding affinity was obtained: a factor of 40 and 20 toward Fe_3O_4 *NPs* and a small boronic acid, FPBA. This versatile strategy can contribute to the synthesis of ultra-strong nitrocatecholic adhesives containing a broad range of counits stable toward nitration procedure.

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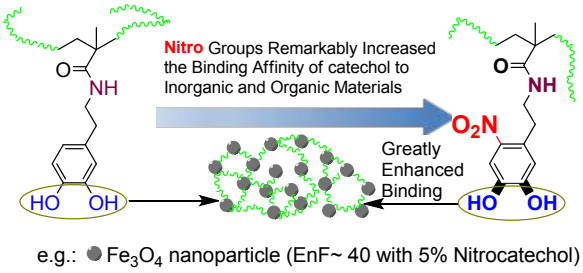

Nitro groups remarkably increased the binding affinity of catechol to inorganic and organic materials.