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REGIOSELECTIVE HRP-CATALYZED POLYMERIZATION OF 4-AMINO-PHENOL

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ABSTRACT

Results on the regioselective enzymatic polymerization of 4-amino-phenol (**1**) are reported. The HRP-catalyzed treatment of unprotected 4-amino-phenol (**1**) with hydrogen peroxide results mainly in the formation of [1,4]benzochinone-monoimine (**6**). In contrast, it was possible to build up phenol polymers, which had relatively high molecular masses, via protection of **1** with 4-nitro-benzaldehyde (**2**) leading to 4-(4-nitro-benzylidenamino)-phenol (**3**). The polymer-analogous deprotection of the phenol polymers was performed by treatment with THF/HCl and confirmed by FT-IR, ^{1}H-NMR and UV-Vis analysis. As a result, electrical conducting poly(4-amino-phenol) was obtained, which should have potential application as a redox active polymer, as shown by cyclic voltammetry measurements. Additionally, detailed studies concerning the structure of the phenol polymers **4** and **5** were performed with ^{1}H-NMR, ^{13}C-NMR and FT-IR spectroscopy. Aborting the polymerization process by adding *bovine liver catalase* at an early stage made it possible to synthesize dimers of *3*. This finding allowed a more precise description of the polymeric structure and provides a clearer view of the polymerization mechanism.

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Key Words: Enzyme; Polyphenol; Redox polymer; Structure; Regioselective

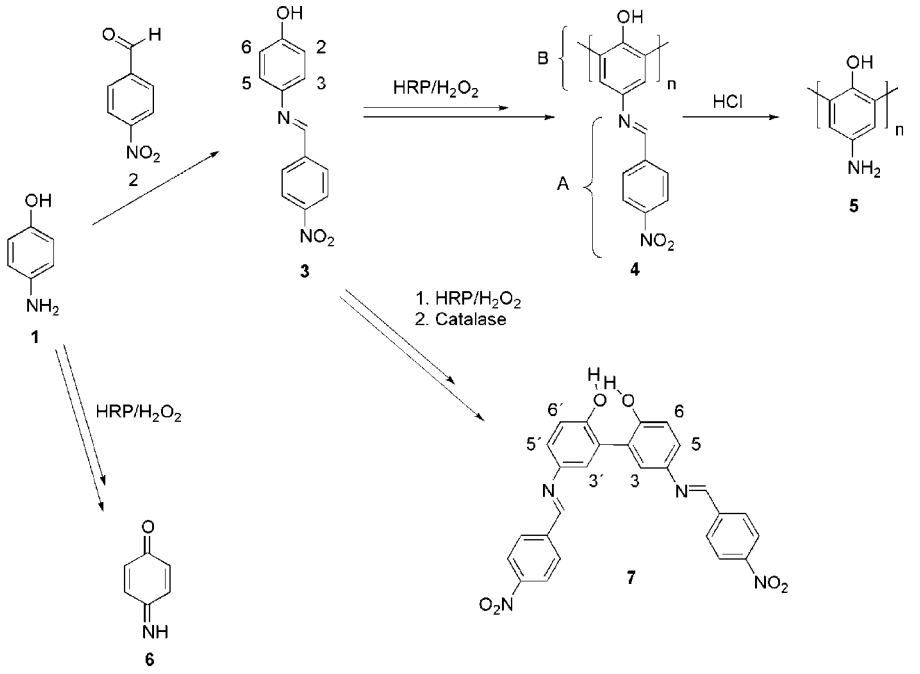
INTRODUCTION

Enzymatically catalyzed polyreactions of some artificial aromatic, electron-rich systems by oxidation mechanism became a potential alternative route to usual chemical polycondensations preferentially performed with formaldehyde.[1] In recent studies, it was demonstrated, that aromatic systems like *p*-substituted and *m*-substituted phenols can be polymerized in the presence of the enzyme *horseradish peroxidase* (HRP)/H_2O_2 as catalyst system to produce polyaromatic compounds.[2–4] Beside our previous interest on the formation of phenol polymers bearing maleimide- or methacryloyl groups in water by use of cyclodextrins[5,6] and the synthesis of photosensitive phenol polymers containing cinnamoyl[7] or nitrone[8] groups, and the detailed study of the formation of copolymers consisting of two different phenol monomers,[9] we have studied an approach to build up new types of phenol polymers based on the commercially available 4-amino-phenol as monomer. The synthesis of polymers from mono-protected hydroquinone was already realized[10,11] and its application as a redox polymer was demonstrated by Dordick et al. The application of similar enzymatically synthesized materials as electrical conducting polymers was shown recently.[12] A synthesis of phenol polymers from 4-amino-phenol has not been reported yet. Thus, we were encouraged to build up redox active phenol polymers of this electron-rich monomer. A detailed structural analysis is usually difficult in the case of phenol polymers. Up to now, the chemical structure of the above mentioned redox active polymers and electrical conducting phenol polymers seems to be still unknown. Therefore, our aim in this work was also to develop a method to analyze the chemical structure of a phenol polymer more accurately.

RESULTS AND DISCUSSION

Synthesis

In order to achieve a selective polyrecombination of 4-amino-phenol with the HRP/H_2O_2 system, the monomer was protected by condensation of the amino group of 4-amino-phenol (**1**) with 4-nitro-benzaldehyde (**2**) as illustrated in Sch. 1. The resulting 4-(4-nitro-benzylidenamino)-phenol (**3**) was used as a starting material for the enzymatic polymerization using mixtures of organic solvents and aqueous buffer solution. The results of these experiments are summarized in Table 1. Before we started to investigate the polymerization experiments, we confirmed by ^{1}H-NMR spectroscopy, that **3** is stable for more than 48 h while stirred in mixtures of 1,4-dioxane and



Scheme 1.

various buffer solutions at given pH-values ranging from 5.5–8.3. On the other hand, we proofed by ^{1}H-NMR spectroscopy, that the 4-amino-phenol can be easily released by stirring **3** for 20 min in THF/HCl solution. Finally, we investigated the reaction behavior of unprotected 4-amino-phenol towards the HRP/H_2O_2 polymerization system.

Table 1. HRP-Catalyzed Polymerization of 4-(4-Nitro-benzylidenamino)-Phenol (3)

Organic Solvent	Buffer	Mn	Mw	Isolated Yield[c]
1,4-dioxane	Acetate pH 5.5	1144	11,992	60
1,4-dioxane	Phosphate pH 7.0	2128	12,322	85
1,4-dioxane	THMA pH 8.3[b]	900	8116	30
1,4-dioxane/toluene[a]	Phosphate pH 7.0	2308	9019	40
1,4-dioxane/DMF[a]	Phosphate pH 7.0	2745	11,790	70
DMF	Phosphate pH 7.0	< 500	< 500	15
NMP	Phosphate pH 7.0	< 500	< 500	10

[a]2 mol of cosolvent (toluene or DMF) per 1 mol of monomer.
[b]THMA = Tris(Hydroxymethyl)-aminomethane hydrochloride.
[c]Isolated by pouring the reaction solution into the 4-fold volume of acetonitrile followed by vacuum filtration with a büchner funnel.

The HRP-catalyzed oxidation reaction of unprotected 4-amino-phenol led mainly to the formation of [1,4]benzochinone-monoimine (**6**), which was identified by characteristic signals for this molecule at 185.0 and 146.3 ppm in the ^{13}C-NMR spectrum and an absorption band at 1667 cm^{-1} in the FT-IR spectrum. Furthermore, a considerable amount of 4-amino-phenol remained non-reacted, as indicated by a typical intensive peak at 151.7 ppm and two strong peaks at 115.8 and 115.6 ppm respectively. In contrast, the polymerization of the *N*-protected 4-amino-phenol **3** led to polymers with a M_n-value of around $2*10^3$ g/mol and a M_w-value of around 10^4 g/mol referred to a polystyrene standard (Table 1). It is well-known, that the molecular weight during a HRP-catalyzed polyrecombination depends on the solvent composition and/or pH-value.[13] In our example, the best results were obtained using the established mixture of 80 vol% 1,4-dioxane and 20 vol% phosphate buffer. The influence of various solvent compositions has been reported especially by S. Kobayashi et al.[14] (1,4-dioxane/buffer, acetone/buffer, methanol/buffer). Here, we evaluated also the influence of small amounts of cosolvents (see Table 1). This might be of interest, since small amounts of a cosolvent like polar DMF and non-polar toluene should influence the formation of aggregates of aromatic phenols formed in the 1,4-dioxane buffer solution, which were already observed.[15] In fact, a significant reproducible effect of a cosolvent addition on the molecular weight and the polydispersity of the corresponding phenol polymers of **3** was evidenced. While the addition of DMF to the 1,4-dioxane/buffer solution leads to a higher molecular weight, polymers were not formed in only a DMF/buffer (80/20, vol%) or in a NMP/buffer (80/20, vol%) solution (see Table 1).

Structure Analysis

The spectroscopic characterization of poly-(4-(4-nitro-benzylidenamino)-phenol) (**4**) bearing the *N*-protecting groups and of the unprotected poly-(4-amino-phenol) (**5**) was performed by use of FT-IR, ^{1}H-NMR, and UV-Vis analysis. The FT-IR spectrum of **4** displays a broad absorption around 3200 cm^{-1} and 1200 cm^{-1} for the OH-group and strong absorptions at 1518 cm^{-1} and 1342 cm^{-1} for the asymmetric and symmetric vibration of the N=O valency of the NO_2-group. While the monomer **3** (Fig. 1, top) exhibits two separate absorptions at 853 cm^{-1} and 833 cm^{-1} for both 1,4-di-substituted aromatic rings (4-nitro-phenyl group and 4-substituted phenol), the spectrum of the polyphenol **4** (Fig. 1, middle) shows only one broad absorption at 852 cm^{-1}. This signal was assigned to the 4-nitro-benzyliden moiety, since it decreased after the removal of the protection groups to give the phenol polymer **5** (Fig. 1, bottom). Thus, the decrease of the intensity of the signal at 833 cm^{-1} during the polymerization of **3** was due to a change of the substitution pattern of the aromatic ring of the phenols due to the

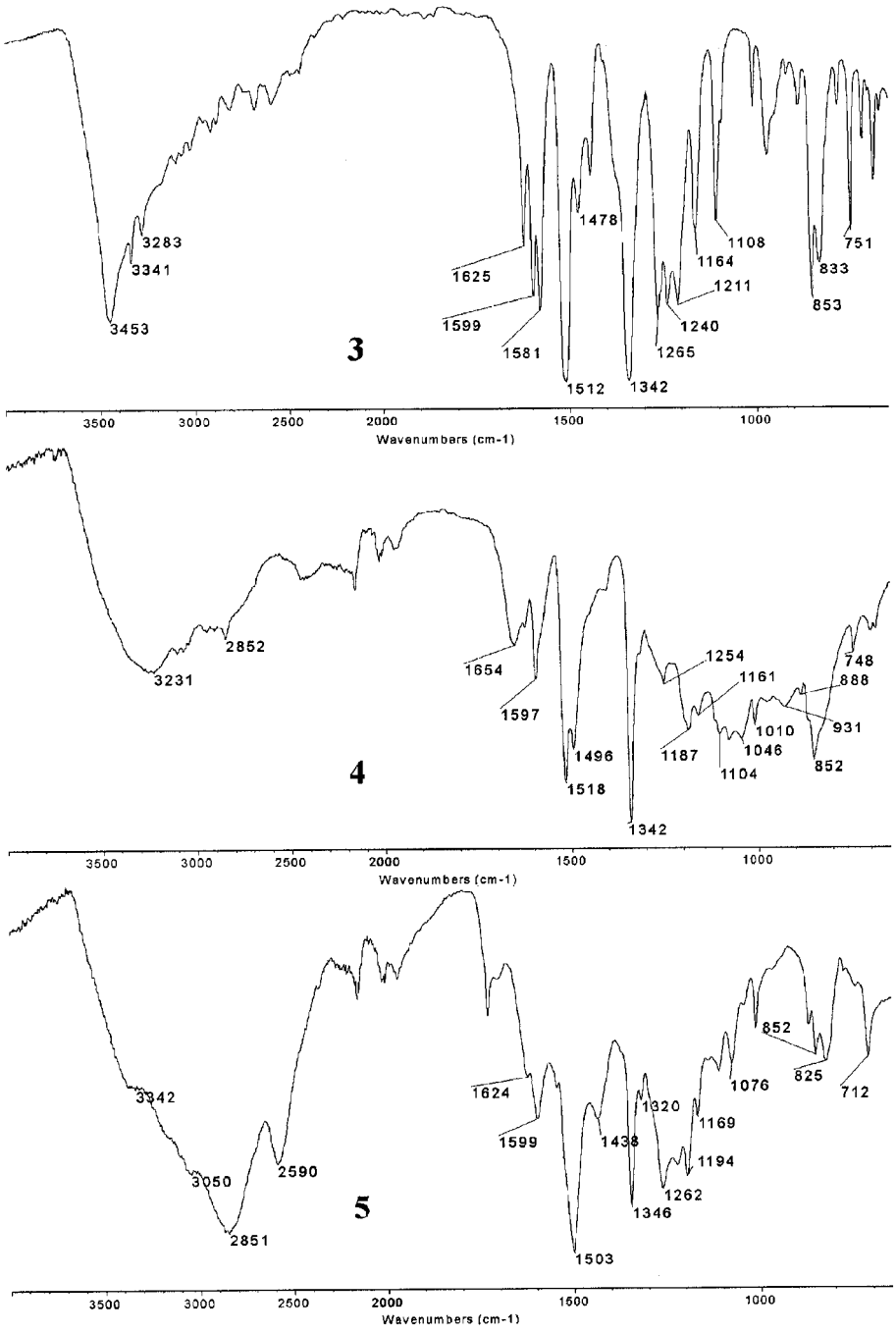


Figure 1. FT-IR spectra (ATR) of 4-(4-nitro-benzylidenamino)-phenol (**3**), poly(4-(4-nitro-benzylidenamino)-phenol) (**4**), and poly(4-amino-phenol) (**5**).

polymerization progress. Note that the formation of *ortho-ortho*-linkages should lead to isolated aromatic protons in *meta*-position. This substitution pattern causes only weak absorptions in the FT-IR spectrum. Therefore, the peak at 833 cm^{-1} should disappear without the appearance of new peaks in the region from 900–700 cm^{-1} as it can be observed in the FT-IR-spectrum of the phenol polymer **4** (Fig. 1). Since new signals corresponding to aromatic ether-bonds cannot be observed in the region from 1170–1100 cm^{-1} in the FT-IR spectra of the phenol polymers **4** and **5**, it seems obvious, that the recombination of the phenoxy radicals, which are believed to be involved in the chain growing process, occurred preferentially at the aromatic ring, not alternatively at the OH-group.

The ^{1}H-NMR measurements also confirmed the formation of *ortho-ortho*-linkages. The 200 MHz ^{1}H-NMR spectrum of the monomer **3** (Fig. 2, top) shows a doublet at 6.83 and 7.30 ppm which can be assigned to the aromatic protons of the phenol moiety. Two further doublets at 8.12 and 8.33 ppm respectively, belong to the aromatic protons of the 4-nitro-benzyliden moiety. The methylidene proton appears as a singlet at 8.78 ppm. In contrast, the ^{1}H-NMR spectrum of the phenol polymer **4** (Fig. 2, bottom), bearing the 4-nitro-benzyliden protection groups, shows only two broad signals. The first one reaches from 6.4 to approximately 7.6 ppm and can be assigned to the aromatic *meta*-protons of the polymer *backbone* (2 per unit in the case of *ortho-ortho*-coupling) and to the *ortho*-protons at the end of the chains. The other broad signal, reaching from 7.7 to 9.2 ppm, corresponds to the aromatic protons and to the methylidene proton of the 4-nitro-benzyliden group (summarizes to 5 protons). The ratio of these two signals was found to depend on the molecular weight, as expected. It is obvious, that with an increase of the molecular weight, the integrated area of the *ortho*-protons at the chain-end of the phenol polymer **4** must decrease relatively to the integrated area of the protons belonging to the protection groups. For a DP of 50, the theoretical ratio of the integral areas is for example 5:2.04. It reaches 5:2 with DP $\rightarrow \infty$, as the number of *ortho*-protons at the chain end approaches 0. The ratio in phenol polymers of higher molecular masses obtained in 1,4-dioxane/buffer at pH-7 reached almost 5:2 (entry 2 in Table 1). The phenol polymer with the lowest molecular weight obtained in NMP/buffer at pH-7 (entry 7 in Table 1) approached a ratio of 5:3, which is the theoretical ratio of a dimer (10 protons of the protection group vs. 6 aromatic protons). These results are in good correlation with the SEC-results in Table 1.

Preparation of Dimers for Structure Analysis

In order to get more detailed information on the structure of the phenol polymers, we analyzed the character of the linkages of enzymatically produced dimers by ^{1}H-NMR and ^{13}C-NMR. In a previous work we

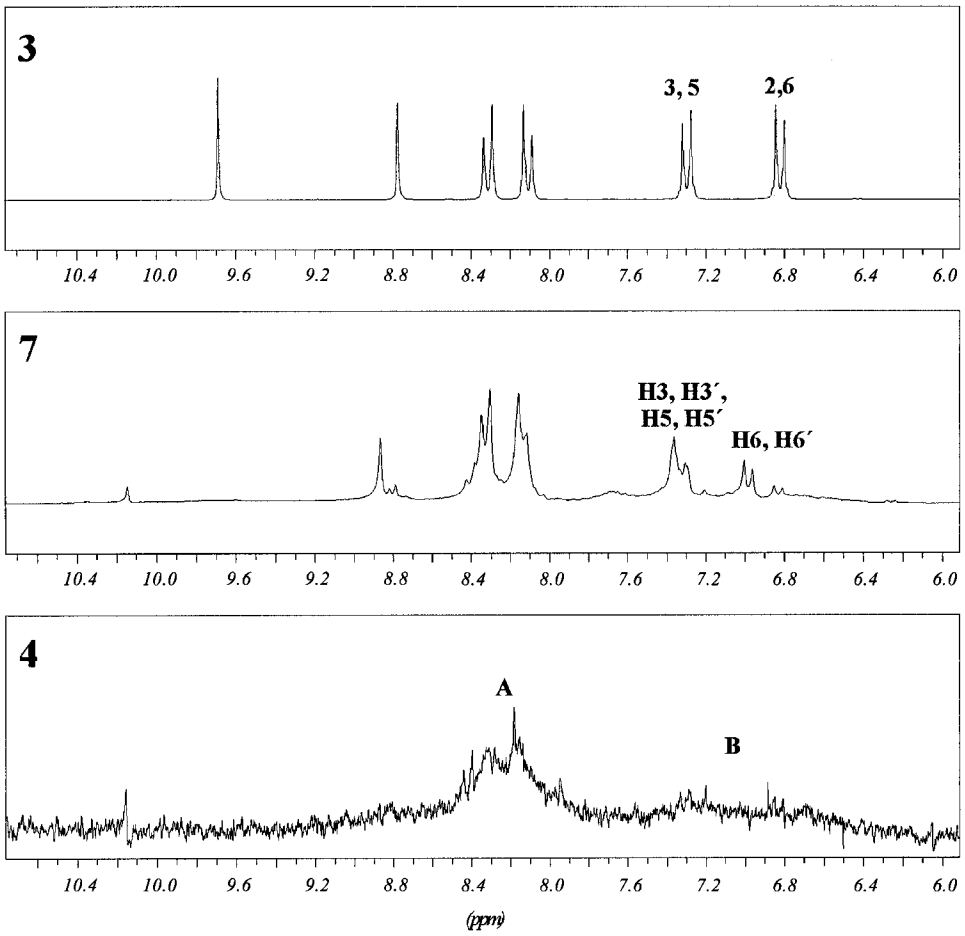


Figure 2. 200 MHz ^{1}H-NMR spectra of 4-(4-nitro-benzylidenamino)-phenol (**3**), 2,2′dihydroxy-5,5′-di-4-(4-nitro-benzylidenamino)biphenyl (**7**), and poly(4-(4-nitro-benzylidenamino)-phenol) (**4**) in DMSO-d_6.

discussed, that the polymerization propagation mechanism involves radical recombination and radical transfer steps,[9] as seen in the literature.[16,17] Moreover, we observed that the polymerization starts with the formation of dimers. This consideration was used to extrapolate the linkage-structure of the phenol polymer **4**. A HRP-catalyzed polymerization of **3** was performed in a 1,4-dioxane/phosphate buffer solution under the same conditions as mentioned before, but after a short reaction time of about 100 min, the polymerization was stopped immediately by adding *bovine liver catalase*. The resulting product **7** was freeze-dried, first analyzed by SEC, and then separated from non-reacted monomer, buffer and enzymes by flash column chromatography. The SEC-analysis showed a M_n-value of 230 g/mol and a M_w-value of 610 g/mol as expected for a mixture of monomers and dimers.

The FD-MS analysis of purified **7** showed one clear signal for a dimer of **3** at $m/z = 483$. A small further signal at $m/z = 349.9$ was assigned to a dimer having one 4-nitro-benzyliden group cleaved due to hydrolysis, which probably occurred during column chromatography. Other signals were not observed. In the ^{1}H-NMR spectrum (Fig. 2, middle), the integration of the signal at 7.00 ppm (H6, H6′) is exactly half of the value reached by the signal at 7.35 ppm (H3, H3′, H5, H5′). The peak pattern of the signal at 7.35 ppm changed also from an AB-system to an ABX-system, thus proving the existence of mainly 2,2′-dihydroxybiphenyl derivatives (**7**). A further small signal at 6.85 ppm is due to the presence of mono-hydrolyzed **7**, which had been already identified by FD-MS. Additionally, the ^{13}C NMR of **7** showed a new peak at 124 ppm for the new formed 1,3-linkages at the *ortho*-positions accompanied by a significant decrease of the signal at 116 ppm, which represented the C2 and the C6 carbons of **3**. In summary, the preparation and analysis of dimers (**7**) by aborting the polymerization at an early stage strongly indicates the existence of *ortho-ortho*-linkages and it can be expected that the further radical coupling to polymers occurs via the same reaction sites as the recombination of the phenoxy radicals to dimers.

Deprotection of 3

The formation of poly(4-amino-phenol) **5** by deprotecting **4** with HCl in THF was proofed by ^{1}H-NMR and FT-IR analysis. During the cleavage reaction of the protection groups, the signal reaching from 7.7 to 9.2 ppm, which belongs to the protons of the 4-nitro-benzyliden group, decreased dramatically, as expected. According to that, the absorptions at 1518 cm^{-1} and 1342 cm^{-1} representing the aryl-NO_2-residue decreased in the FT-IR spectrum of **5**. In order to quantify the deprotection of the phenol polymer **4**, UV-Vis-analysis was performed in THF, which allowed sufficient UV-Vis-measurements at wavelengths above 220 nm From Fig. 3, which shows the UV-Vis-spectra of 4-amino-phenol (**1**), 4-nitro-benzaldehyde (**2**) and **3,** it is identifiable that the imine-structure causes an absorption maximum at 380 nm, which is not visible at either 4-amino-phenol, nor the 4-nitro-benzaldehyde. Thus, the presence of this absorption maximum in the UV-Vis-spectrum of phenol polymer **4**, displayed in Fig. 4, is clear evidence for the unchanged structure of the protection groups in this polymer. The quantitative deprotection of this compound was proofed by the UV-Vis spectrum of the resulting compound **5**, which does not show an absorption around 380 nm (Fig. 4).

Redox Properties

The electrochemical behavior of **5** was analyzed by performing cyclic voltammetry of a thin film from **5** on a glassy carbon electrode in aqueous

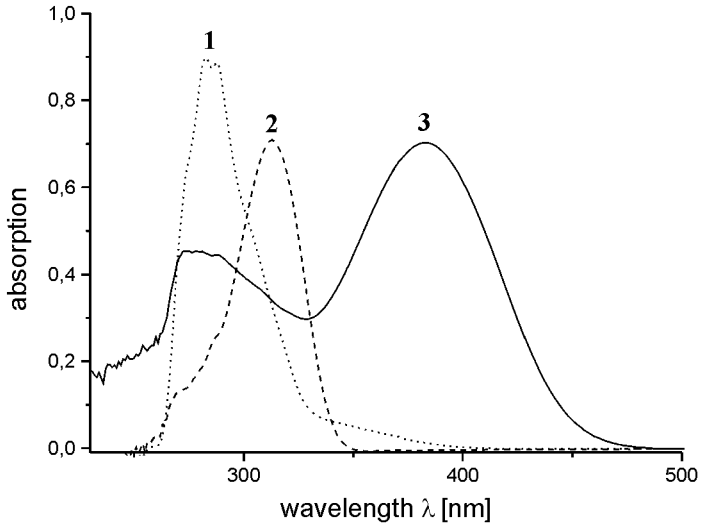


Figure 3. UV-Vis spectra of 4-aminophenol (**1**), 4-nitro-benzaldehyde (**2**), and 4-(4-nitro-benzylidenamino)-phenol (**3**) in THF.

buffer solutions. The redox properties were found to depend on the pH, as expected. Clear oxidation and reduction peaks were detected in 0.1 M H_2SO_4 at 580 mV and 380 mV respectively. The change of the pH from 5.5 to 8.3 resulted in shifts of both peaks to lower voltage (Fig. 5). This indicates the reversible oxidation of the 4-amino-phenol units of **5**, which occurs easier at

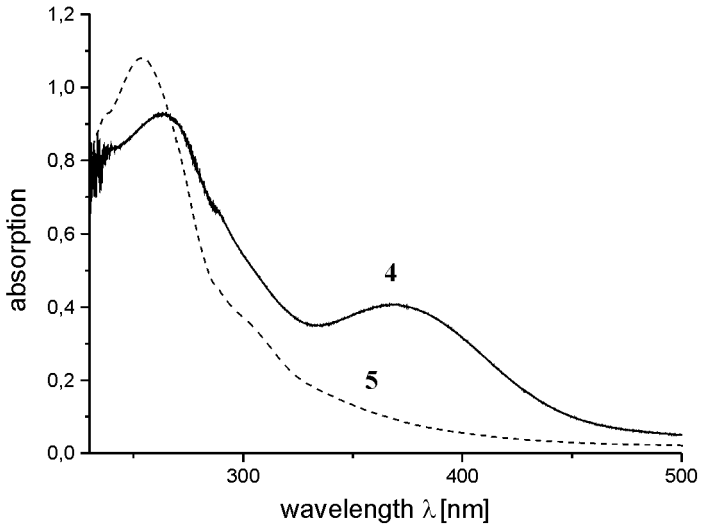


Figure 4. UV-Vis spectra of poly(4-(4-nitro-benzylidenamino)-phenol) (**4**) and poly(4-amino-phenol) (**5**).

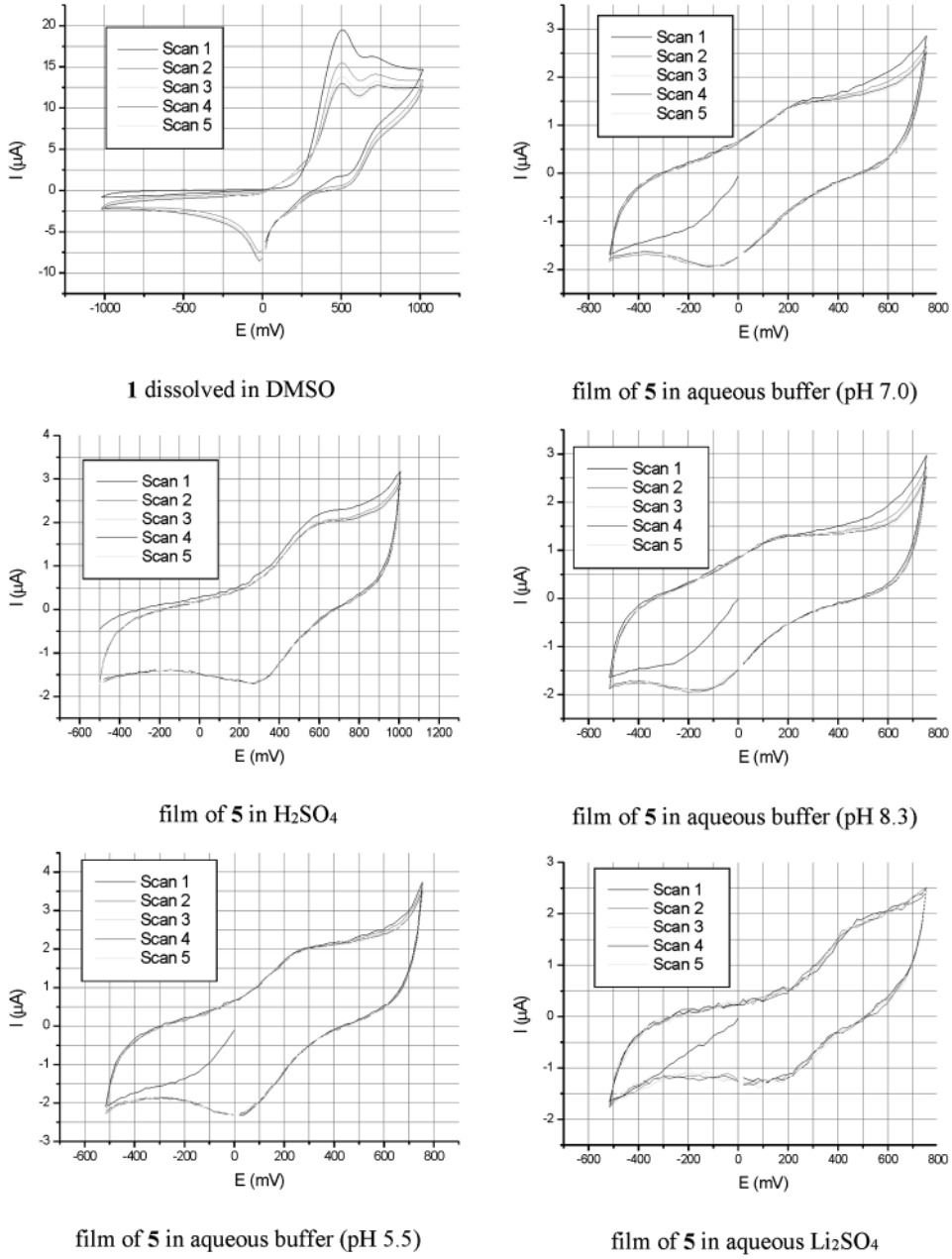


Figure 5. Cyclic voltamograms of 4-aminophenol (**1**) (0.01 M) dissolved in DMSO containing tetrabutylammonium hexafluorophosphate (0.1 M) compared to a film of poly(4-amino-phenol) on a glassy carbon electrode (**5**) in aqueous Li_2SO_4 (0.1 M) and in different aqueous buffer solutions. The buffer solutions contained $KClO_4$ (0.1 M).

higher pH-values, as the phenol groups are then present as phenolates. It can be assumed, that a $2e^-/2H^+$ transfer leading to 4-imino-2,5-cyclohexadien-1-one units occurs. However, the cyclic voltamogram of **1** shows two separate peaks, which were not observed in the curves of the polymer films. This might be caused by low resolution only. It can be observed in all cyclic voltamograms, that the redox behavior is stable, and the curves did not change during several hundred cycles. It was also possible to store the film on the electrode under argon for several weeks, without any changes in the redox behavior according to the cyclic voltamograms.

EXPERIMENTAL

Materials

Horseradish-Peroxidase (691 U/mg) was purchased from BioChemika. All solvents of p.a. quality (Riedel de Haen) were stored over molecular sieves 3 or 4 Å. Technical solvents for flash chromatography were distilled. All other chemicals were purchased from Acros or Fluka and used without further purification. Silica gel for column chromatography was purchased by Baker (30–60 μm particle size).

Preparation of 4-(4-Nitro-benzylidenamino)-Phenol (3)

10 g (66.2 mmol) 4-nitrobenzaldehyde and 11.2 g (66.2 mmol) 4-amino-phenol and 0.2 g 4-toluenesulfonic acid were suspended in 200 mL of chloroform. The mixture was refluxed for 4 h using a water separator. The mixture was then cooled and the yellow-orange solid was filtered off. Washing with acetone and recrystallization from methanol gave the product with sufficient purity. Depending on the quality of 4-amino-phenol however, a column chromatography using silica gel and EtOAc/petrol ether (1:1) as eluent is recommended. The yield was 87% of an orange colored solid: mp 152°C; R_f 0.86 (ETOAc, petroleum ether 1:1 vol.); FT-IR (ATR) 3453 (OH); 1625; 1599 (C=N); 1581; 1512 (aryl); 1342 (NO_2); 1265; 1240; 1211 (C-OH); 1164; 1108 (C-O); 973; 853 (aryl); 833; (phenol); 751; 690 cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 9.69 (s, 1H, OH); 8.78 (s, 1H, NC=H); 8.32 (d, 2H, H3, H5-phenyl, $J = 8.78$ Hz); 8.11 (d, 2H, H2, H6-phenyl, $J = 8.78$ Hz); 7.30 (d, 2H, H3, H5-phenol, $J = 8.78$ Hz); 6.82 (d, 2H, H2, H6-phenol, $J = 8.78$ Hz); ^{13}C NMR (100.6 MHz DMSO-d_6) δ 157.21 (N=CH); 154.61 (C1-phenol); 148.29 (C4-phenyl); 142.01 (C4-phenol); 141.58 (C1-phenyl); 128.99 (C2, C6-phenyl), 123.87 (C3, C5-phenol); 123.06 (C3, C5-phenyl); 115.76 (C2, C6-phenol). Anal. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56; O, 19.82. Found: C, 64.23; H, 4.37; N, 11.64; O, 19.76.

Preparation of the Polymer 4

Each peroxidase-catalyzed polymerization of **3** was carried out in a mixture of 80 vol% 1,4-dioxane and 20 vol% aqueous buffer solution with 0.1 M monomer, equimolar amount H_2O_2 and 0.15 mg/mL HRP. The phenol was first dissolved in the organic solvent. If an organic cosolvent was used, it was added to the organic solvent at the beginning. The calculated amount of solid enzyme was then dissolved into a suiTable amount (here: 5 mL) of buffer solution. The rest of the buffer solution was added to the organic solvent while shaking the flask, and then the enzyme solution was added. The calculated amount of H_2O_2 (30% solution in water) was added 20 times in 15 min intervals. Polymers were collected after 24 h by pouring the reaction mixture slowly into the 4-fold volume of acetonitrile followed by vacuum filtration with a büchner funnel.

Preparation of Polymer 5

1.5 g of polymer **4** was dissolved into 100 mL THF and the solution was set under an argon atmosphere. To the dark brown solution, 15 mL of HCl (37%) were added and the solution was stirred for 2 h. The THF-solution was concentrated in vacuum and the residue suspended under argon atmosphere in ethyl acetate. The dark solid of polymer **5** was collected by vacuum filtration, followed by intensive washing with ethyl acetate in almost quantitative yield.

Preparation of the Dimer 7

A peroxidase-catalyzed polymerization of **3** was performed in a mixture of 80 vol% 1,4-dioxane and 20 vol% aqueous buffer solution with 0.1 M monomer and 0.15 mg/mL HRP as described above for the preparation of **4**. The polymerization was stopped after 100 min of reaction time by adding *catalase* from bovine liver in excess. The solvents were removed in vacuum, and the product separated from 4-aminophenol, buffer and enzymes by flash column chromatography using a gradient of hexane/ethyl acetate as eluent.

Cyclic Voltammetry

2 μL of a 2% (w/w) solution were spread onto the surface of an glassy carbon electrode (Metrohm, disk diameter: 2.0 mm), which have been pretreated according to standard procedures with Al_2O_3. The solvent was evaporated at 40°C in a drying oven equipped with a vacuum pump to give a thin film on the electrode.

Other Measurements

NMR spectra were recorded on a Bruker AM400 FT-NMR-spectrometer (400 MHz) or on a Bruker AC200 FT-NMR-spectrometer (200 MHz). IR-spectra were run on a Nicolet 5SXB (MCT-detector, ATR) or a 5DXC (DTGS-detecor) FT-IR-spectrophotometer. SEC-measurements were performed using a PSS apparatus with a Knauer refractive index (RI) detector and a TSP UV2000 UV-Vis detector at 25°C under the following conditions: PSS-HEMA 10 μ, 40, 100, 3000 Å porosity and DMF containing 0.1% LiBr at 75°C as eluent at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained using PSS polystyrene standards (374-10^6 D). UV-Vis analysis was performed with a Unicam UV540 UV-Vis spectrometer. Elemental analyses were carried out with a Foss Heraeus vario EL. A Mettler Toledo FP62 apparatus was used for measuring melting points.

CONCLUSION

The regioselective enzymatic polymerization of 4-amino-phenol (**1**), was realized by forming an azomethin (**3**) before polymerization and subsequently polymer-analogous deprotection of the obtained poly-[4-(4-nitro-benzylidenamino)-phenol] (**4**) to give poly-(4-amino-phenol) (**5**). A film of this polymer showed a stable, reversible and pH-depending redox behavior. By aborting the polymerization process at an early stage, it was possible to synthesize dimers of 4-(4-nitro-benzylidenamino)-phenol (**3**). The existence of mainly 2,2′-dihydroxybiphenyl derivatives (**7**) as resulting products supports the proposed 1,3-phenylen linkages of the polymer structure. Moreover, this proofed, as found in our previous work, that at the beginning of the polymerization the main process is the formation of dimers only, which almost certainly subsequently undergo radical transfer and recombination processes, as supposed in literature.

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