Controlled Free-Radical Polymerization of Phenol Derivatives by Enzyme-Catalyzed Reactions in Organic Solvents

Madhu S. Ayyagari,[†,‡] Kenneth A. Marx,[‡] Sukant K. Tripathy,[‡] Joseph A. Akkara,[†] and David L. Kaplan*[,†]

Biotechnology Division, U.S. Army Natick RD&E Center, Kansas Street, Natick, Massachusetts 01760, and Centers for Advanced Materials and Intelligent Biomaterials, Department of Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts 01854

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ABSTRACT: The ability to control the molecular weight and dispersity of poly(*p*-ethylphenol) was demonstrated. The polymer was synthesized enzymatically in different organic solvents and a water-in-oil microemulsion. Using solubility parameters, the composition of the reaction medium was varied to study effects on the polymer yield, molecular weight, and dispersity. As a result, polymers with low dispersities and molecular weights from 1000 to 3000 could be synthesized in reversed micelles. In comparison, reactions in bulk solvents resulted in a narrow range of molecular weights (281–675). With dimethylformamide as eluent, the effect of LiBr on the molecular aggregation of poly(*p*-ethylphenol) was studied using gel permeation chromatography. The presence of LiBr (at ≥0.35 w/v %) in dimethylformamide resulted in complete dissociation of the aggregation in solution. Poly(*p*-ethylphenol) was functionalized at hydroxyl positions with palmitoyl and cinnamoyl groups. Structural characterization of the polymers was carried out by ^{13}C-NMR, UV, and FTIR spectroscopies.

Introduction

Peroxidase-catalyzed free-radical polymerization of phenol and its derivatives is well documented.[1-5] The enzyme-mediated synthesis of polyphenols offers a viable alternative to the currently used chemical synthesis of such commercial phenolic resins as Novalak prepared from phenol and formaldehyde. The use of formaldehyde in the chemical industry is limited because of its toxicity.[6] Horseradish peroxidase (HRP) is the most widely used biocatalyst in the polymerization of phenol, aniline, or their derivatives. HRP has been shown to be active in a number of organic solvents or solvent mixtures,[1,2] and the reaction is typically initiated by the addition of hydrogen peroxide as an oxidant. Dordick *et al.*[1] used HRP in a dioxane/water system to prepare a number of polymers and copolymers from various phenolic monomers. Akkara *et al.*[2] prepared polymers and copolymers of various phenols and aromatic amines using these reactions and carried out detailed characterization of the polymer products. *p*-Alkylphenols were also polymerized at oil–water (reversed micelles) and air–water (Langmuir–Blodgett trough) interfaces.[3,7] Because of their amphiphilic nature, the alkylphenols are positioned at the interface, and in the presence of HRP and hydrogen peroxide the monomers are oxidatively coupled to form polymers. The poly(*p*-alkylphenols) prepared in reversed micelles were shown to exhibit relatively more uniform molecular weight distributions than those prepared in bulk organic solvents.[3]

Polymers of phenols and aromatic amines have found wide application in a number of areas such as coatings, laminates, and photoresists.[4,8] Besides possessing good thermal properties, these polymers can be doped to make them electrically conductive.[7] However, the molecular weight distribution of polyphenols, which can significantly influence functional properties, has not been extensively explored. This paper addresses fundamental issues involved in the control of molecular weight and dispersity of the polymers, as well as detailed structural characterization of the polymers. The study was conducted with a few commonly used organic solvents and their mixtures, and their effect on enzyme activity and solubility of growing polymer chains was investigated.

Materials and Methods

(i) Chemicals. Isooctane (J.T. Baker, Phillipsburg, NJ) and chloroform (Fluka, Ronkonkoma, NY) were stored with molecular sieves to remove water from the solvents. 1,4-Dioxane, acetonitrile, and *N*,*N*-dimethylformamide (DMF) (American Bioanalytical, Natick, MA) were used as received. All solvents were of HPLC grade. Dioctyl sodium sulfosuccinate (AOT), 30% hydrogen peroxide (w/w), HEPES buffer, and the monomers were supplied by Aldrich Chemical Co. (Milwaukee, WI). The enzyme horseradish peroxidase (Type II) was purchased from Sigma Chemical Co. (St. Louis, MO). Polystyrene standards were purchased from Waters Associates (Milford, MA).

(ii) Reactions. A typical reaction was carried out in reversed micelles as follows. A 10-mL solution of 0.15 M AOT in isooctane was prepared, and 0.4 mL of an aqueous preparation of HRP (12.5 mg/mL) was added to form a clear reversed-micellar solution of a W_0 (molar ratio of water to surfactant) of about 15. *p*-Ethylphenol was added to the reversed-micellar solution, and the reaction was initiated by adding drops of hydrogen peroxide (up to about 30% stoichiometric excess) while stirring the reaction mixture. The reaction was exothermic with rapid formation of a yellowish precipitate. After continuing the stirring for a few more hours, the precipitate was centrifuged and washed a few times with pure isooctane to remove the surfactant and any unreacted monomer. The final precipitate was dried overnight under reduced pressure at 50 °C.

In cases where a mixture of chloroform and isooctane was used to form reversed micelles, the same procedure was followed except that the corresponding solvent mixture was used in place of isooctane. However, stable (i.e., transparent and single phase) reversed-micellar solutions were found to be difficult to form with a mixture of chloroform and isooctane. A stable microemulsion could be obtained only up to a W_0 of 7 with 100% chloroform at room temperature, and phase separation occurred at higher values.

* Corresponding author.
† U.S. Army Natick RD&E Center.
‡ University of Massachusetts Lowell.
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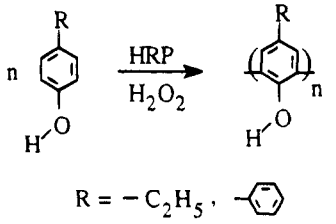

R = $-C_2H_5$, -⬡

Figure 1. Schematic of para-substituted phenol polymerization catalyzed by horseradish peroxidase (HRP).

In the absence of reversed micelles, reaction mixtures were prepared by first dissolving the monomer and the enzyme in a mixture of buffer and solvent such as DMF. The reaction was initiated, as before, by the dropwise addition of hydrogen peroxide. The enzyme was completely soluble at 0.5 mg/mL concentration in DMF/water mixtures at all solvent compositions studied.

(iii) Characterization. Thermal characterization of polymers was carried out on Du Pont thermal analyzers (TA Instruments, Inc., New Castle, DE). For differential scanning calorimetry (DSC) analysis, the polymers were hermetically sealed and heated under a nitrogen atmosphere at a temperature gradient of 10 °C/min from room temperature to 300 °C. Thermogravimetric analysis (TGA) was carried out at the same temperature gradient and under a nitrogen atmosphere but heated to 600 °C. Molecular weights were determined on a Waters LC Module I instrument (Millipore, Milford, MA) with an on-line gel permeation chromatography (GPC) column (GBR mixed-bed linear column with a molecular weight range of 100 to over 200 million; Jordi Associates, Inc., Bellingham, MA). A UV detector at 270 nm was used to detect the polymer. The GPC data were collected and processed with Milleniun GPC software supplied with the instrument. An eluent flow rate of 1 mL/min was maintained under isocratic conditions. Narrow molecular weight polystyrene standards were used for calibration. All samples were filtered through 0.2 μm PTFE filters (Lida, Kinosha, WI) prior to injection. It was ascertained that the filters did not retain any polymer during filtration.

For GPC analysis, poly(*p*-ethylphenol) was completely dissolved at a concentration of 1 mg/mL in a series of DMF-based solutions with varying LiBr concentrations in the range of 0–1% (w/v). A given composition (between 0 and 1% LiBr/DMF) of the GPC solvent was prepared by mixing pure DMF and 1% LiBr/DMF in appropriate proportions. For all injections, the compositions of the GPC solvent and the solvent used to prepare the sample for injection were identical. A mixture of polystyrene standards (122 to 2.7 million; narrow distribution with polydispersity in the range of 1.02–1.2) was prepared in all compositions of LiBr and DMF and always injected before analyzing the polyphenol sample in the corresponding solvent.

^{13}C-NMR spectra on the monomer and polymer were recorded on a 200-MHz Varian instrument (^{13}C broad-band probe, Model XL-200, Palo Alto, CA). Deuterated acetone and tetramethylsilane (TMS) were used as the solvent and the internal standard, respectively. Infrared spectra were recorded on a Perkin-Elmer 1760 FTIR–FT Raman spectrophotometer (Norwalk, CT) at 4-cm^{-1} resolution. The samples were cast as thin films on a KBr window from chloroform solutions. UV spectroscopy studies were carried out on a Beckman DU 7500 spectrophotometer (Beckman Instruments, Inc., Fullerton, CA).

Results and Discussion

Figure 1 illustrates the reaction scheme and the structures of monomers used in this study. Other phenol derivatives were also polymerized, and the results will be reported soon.[10] Cross-linking in polymer structure is expected in those cases where the ortho and para positions in the corresponding monomer structure are unsubstituted, as is the case with *p*-phenylphenol (at 2′, 4^0, and 6′). ^{13}C-NMR studies on poly(*p*-ethylphenol) indicate that the linkage between any two

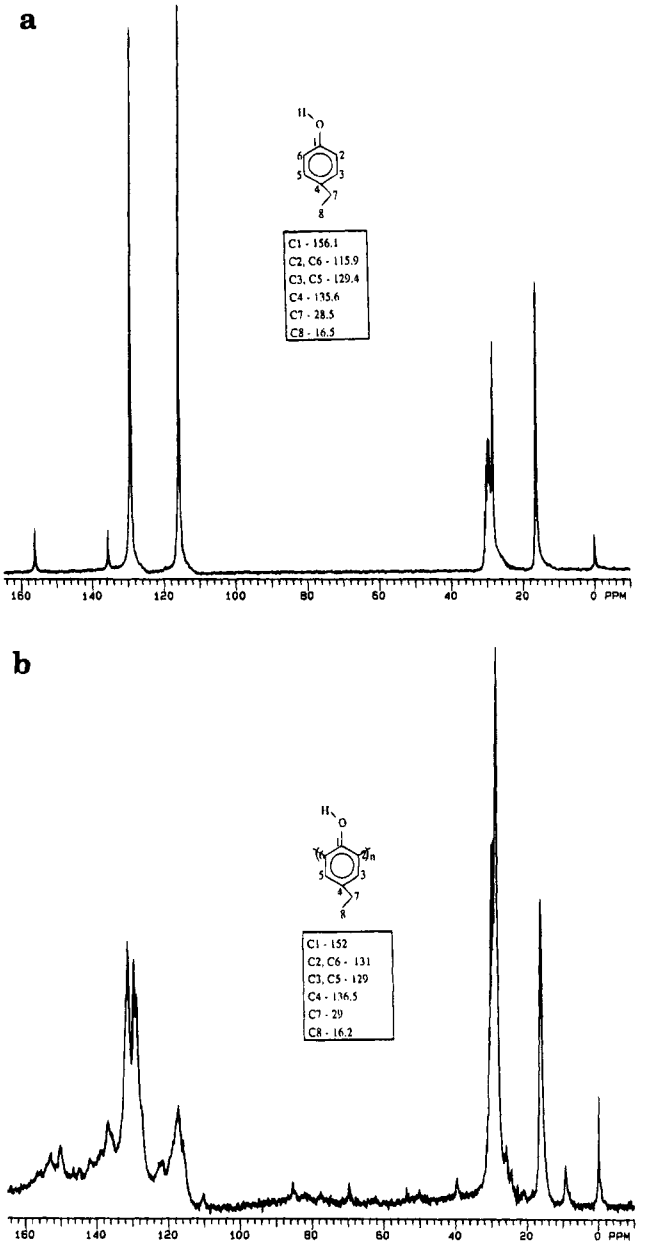

Figure 2. (a) ^{13}C-NMR spectrum for *p*-ethylphenol. (b) ^{13}C-NMR spectrum for poly(*p*-ethylphenol).

adjacent phenyl rings is largely at ortho positions (Figure 2a,b). However, this type of linkage may strain the polymer backbone in such a manner that the phenyl rings are out of plane with respect to the adjacent rings. As a result, the polymer backbone may be forced into a coiled structure. To support this notion, molecular dynamics studies are underway.

Parts a and b of Figure 2 illustrate ^{13}C-NMR spectra and peak assignments for the monomer and the polymer, respectively. The peak for C2 and C6 (at 115.9 ppm in the monomer and 117 ppm in the polymer) diminished, while an additional peak appeared at 131 ppm in the polymer. The peak position at 131 ppm is in agreement with the theoretically calculated peak position for ortho linkages on the ring. On the other hand, if the monomer were linked at meta positions on the ring, the peaks for C3 and C5 should shift downfield from 129.4 ppm in the monomer to 144 ppm in the polymer. However, the polymer spectrum in Figure 2b shows no such peak ruling out linkages at meta positions. There was no significant change in the peak

position for C4 ruling out ether linkages. Although the hydroxyl groups are involved in the formation of free radicals leading to polymer formation, they do not appear to be involved in bond formation. In addition, previous infrared studies revealed no ether linkage in the polymer structure.[9] Thus the phenyl rings in the polymer appear to be linked primarily at ortho positions.

(a) Effect of LiBr on Molecular Association. Dimethylformamide is a good solvent for solution studies of polyphenols. Earlier reports[1-3] used a mixture of DMF and methanol, at a ratio of 4 to 1, as a GPC solvent in the determination of molecular weights of polyphenols. DMF is an interesting solvent, especially for polyhydroxy compounds such as polysaccharides and polyphenols. For example, amylose is not soluble in DMF, but the polysaccharide swells as DMF penetrates into and "wets" the polymer. However, it is well-known that, in the presence of about 3% (w/v) LiBr, amylose could be dissolved at a concentration of about 1% (w/v) in DMF.[10] Polyphenol, like a polysaccharide, is also a polyhydroxy compound. Although DMF easily dissolves poly(*p*-ethylphenol), there still may be inter/intramolecular associations in the polymer. These interactions may result in an apparently high molecular weight in GPC analysis. A systematic study was undertaken to determine the effects of LiBr on aggregation phenomena as reflected by the weight-average molecular weight of poly(*p*-ethylphenol).

Dordick *et al.*[1] identified the potential aggregation of polyphenol molecules and used a mixture of DMF and methanol to break the association. Molecular weights in the range of a few hundred to a few thousand were reported for a number of different polyphenols, with poly(*p*-phenylphenol) exhibiting a molecular weight of 26 000. Using an identical GPC solvent composition, Akkara *et al.*[2] reported molecular weights of over 400 000 for poly(*p*-phenylphenol) prepared in a dioxane/water system. Rao *et al.*[3] reported an average molecular weight of about 20 000 with a DMF/methanol solvent mixture as the GPC eluent for poly(*p*-ethylphenol) prepared in AOT reversed micelles. However, it is not clear if the solvent mixture of DMF and methanol at a 4:1 ratio is optimal to deaggregate the polymer chains and give a true molecular weight. To address this problem, the molecular weights of poly(*p*-ethylphenol) prepared in reversed micelles and a dioxane/water system and poly(*p*-phenylphenol) prepared in a dioxane/water system were analyzed as a function of LiBr concentration in DMF and a DMF/methanol mixture as GPC eluents.

Figure 3 illustrates the effect of LiBr concentration in DMF as the GPC eluent on the weight-average molecular weight of poly(*p*-ethylphenol) prepared in reversed micelles. There was a dramatic decrease in the molecular weight by over 3 orders of magnitude when the LiBr concentration was increased from 0 to 0.35%. The molecular weight and dispersity of the polymer stabilized at about 2500 and 1.36, respectively, above 0.35% LiBr in DMF. Above this critical concentration of LiBr in DMF, there is no additional effect on the polymer molecular weight.

An analogous phenomenon was observed with the solubility studies of amylose in DMF.[10] Although DMF is capable of forming its own hydrogen bonds with the polysaccharide (as noted earlier, the polysaccharide swells in DMF but is insoluble), it may not be able to completely disrupt the intermolecular forces. However, LiBr appears to be very effective in overcoming these

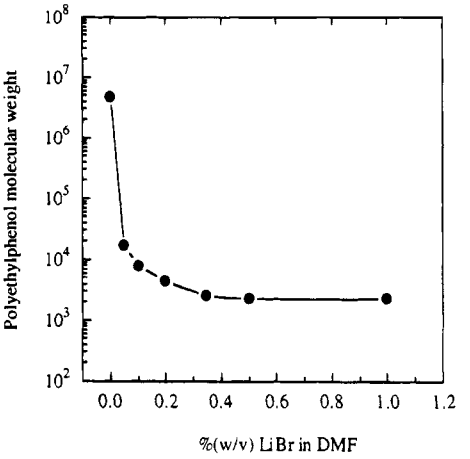

Figure 3. Effect of LiBr concentration on poly(*p*-ethylphenol) molecular weight.

intermolecular interactions. The polysaccharide becomes soluble at a concentration of 3% LiBr in DMF. It is possible that the solubility of the polyhydroxy compound is dictated by a fixed ratio between the amylose and LiBr concentrations in DMF. The same argument applies to the molecular dissociation of poly(*p*-ethylphenol) in the presence of LiBr in DMF. Not unexpectedly, there was no effect of LiBr on the retention times of the polystyrene standards due to the lack of strong interchain interactions.

A mixture of DMF/methanol at a 4:1 ratio was also used as the GPC solvent to determine the molecular weight of poly(*p*-ethylphenol) synthesized in AOT/isooctane reversed micelles. The result was a bimodal distribution with average molecular weights of 90 000 and 300 000 for the two distributions. A similar bimodal molecular weight distribution was described by Akkara *et al.*[2] for poly(*p*-phenylphenol). Molecular aggregation is still significant in this solvent system since the molecular weight of the sample dropped to about 2700 in the presence of 1% LiBr in a DMF/methanol mixture at a 4:1 ratio. Identical observations were made with a sample of poly(*p*-ethylphenol) synthesized in a 85% dioxane/water system. Subsequently, a sample of poly(*p*-phenylphenol), synthesized in 85% dioxane/water, was analyzed for molecular weight in both DMF and a DMF/methanol mixture at different LiBr concentrations. As before, the polymer molecular weight dropped from well over 6 million to about 3400 on increasing the LiBr concentration from 0 to 1% (w/v) in DMF. Similarly, poly(*p*-phenylphenol) showed a significant shift to lower molecular weight as the LiBr concentration in a DMF/methanol mixture at a 4:1 ratio was varied in the same concentration range as in DMF. In this case, the molecular weight dropped from about 500 000 to 3200. Table 1 lists some of the above observations. Poly(*p*-ethylphenol) synthesized in reversed micelles exhibited a polydispersity of less than 1.4, and that prepared in bulk solvent, dioxane/water, >2. The average molecular weight of the polymer increased slightly as the surfactant concentration was increased, a phenomenon noted earlier.[3]

The thermal properties of *p*-ethylphenol and poly(*p*-ethylphenol) prepared in reversed micelles are illustrated as DSC and TGA thermograms in parts a and b of Figure 4, respectively. The polymer was reasonably stable until a temperature of about 250 °C, with a loss of less than 10% of the material (6% loss occurred at 200 °C presumably in part due to loss of water). The

Table 1. Molecular Weight and Dispersity Profiles of Poly(*p*-ethylphenol) and Poly(*p*-phenylphenol) Synthesized under Different Conditions as a Function of GPC Solvent Composition

sample	synthesis medium	M_w (Mw/M_n)[a] (a)	(b)	(c)	(d)
poly(*p*-ethylphenol)	AOT/isooctane reversed micelles	>4.5 million (>2.5)	2500 (1.4)	300 000 (>2.0)	2700 (1.4)
poly(*p*-ethylphenol)	85/15 dioxane/water	>6.0 million (>2.5)	3400 (>2.0)	500 000 (>2.0)	3200 (>2.0)
poly(*p*-phenylphenol)	85/15 dioxane/water	>6.0 million (>2.5)	3000 (>2.0)	300 000 (>2.0)	3200 (>2.0)

[a] Molecular weights were determined with GPC solvents (a) DMF, (b) 1% LiBr in DMF, (c) 4:1 DMF/methanol, and (d) 1% LiBr in 4:1 DMF/methanol.

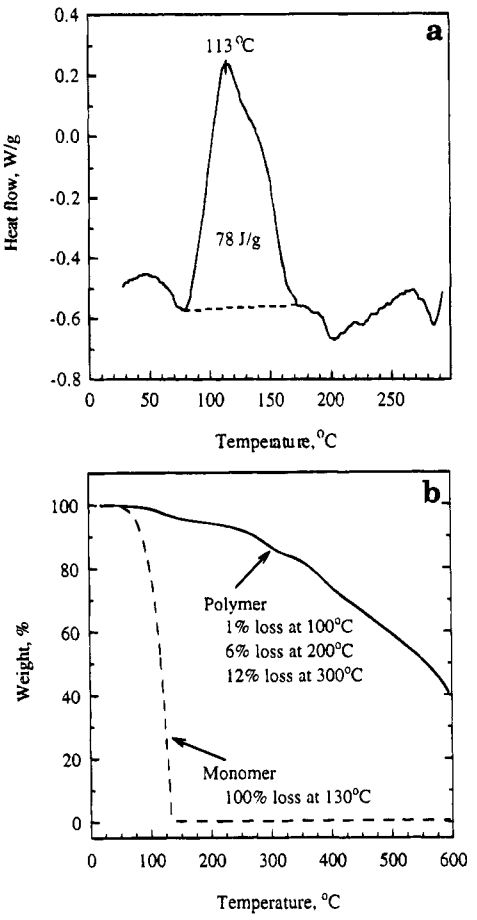

Figure 4. (a) Differential scanning calorimetry (DSC) thermogram of poly(*p*-ethylphenol) prepared in reversed micelles. (b) Thermogravimetric analysis (TGA) of *p*-ethylphenol and poly(*p*-ethylphenol) prepared in reversed micelles.

exotherm at about 110 °C in the polymer DSC thermogram may be due to cross-linking in the polymer or due to loss of heat of crystallization. Once heated over 200 °C, the exotherm was irreversibly lost.

A 170% increase in molecular weight was observed, presumably due to cross-linking, when a sample of poly(*p*-ethylphenol) was heated to 150 °C, and the polymer became significantly more polydisperse than the corresponding untreated polymer. Figure 5 shows portions of the GPC profiles of poly(*p*-ethylphenol) before and after heating the polymer to 150 °C. Both samples were easily soluble in a 1% LiBr/DMF solution that was used as the eluent. X-ray diffraction studies on the samples revealed a partial crystallization of the heat-treated polymer.

(b) Effect of Solvent on the Enzyme Activity and Polymer Molecular Weight. Phenol polymerization was carried out in a mixture of DMF and water at various ratios to investigate the solvent effect on the enzyme activity and on the polymer molecular weight. The objective here was to investigate if the molecular

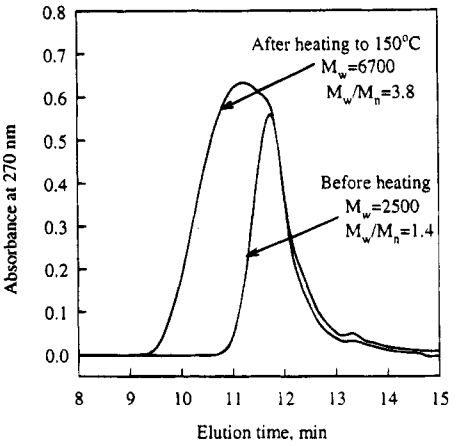

Figure 5. Effect of heating on poly(*p*-ethylphenol) molecular weight.

Table 2. Ranges of Solubility Parameters and Dielectric Constants Covered by the Solvent Systems Used for Polymerization Reactions

solvent system	solubility param ($MPa^{1/2}$)	dielectric constant
isooctane/chloroform	14–19	2–5
DMF/water	25–48	37–78
1,4-dioxane/water	20–48	30–78

weight of polyphenols could be controlled, while maintaining a reasonably narrow distribution, by varying reaction system parameters such as time of reaction, hydrogen peroxide concentration, and solvent composition. Earlier attempts to control the polymer molecular weight by varying the time of reaction or hydrogen peroxide concentration were unsuccessful in reversed micelles and bulk solvents.[10] The initial hydrogen peroxide concentration was found to be stoichiometrically proportional to the monomer conversion, a hallmark of stepwise polymerization and a phenomenon observed previously,[3] and there was no effect on the polymer molecular weight.

The solvent mixtures used in this study, and listed in Table 2, were selected on the basis of the range of solubility parameters that they cover. The wide variation in solubility parameters and dielectric constants for each system was similar to that found in certain supercritical fluids as a function of pressure.[11] Not only do these properties influence the solubility of the growing polymer chain in the corresponding reaction medium, but also the enzyme activity is significantly affected. However, unlike in supercritical fluids, the solvent properties can be varied at ambient conditions of pressure and temperature.

The reaction medium composition was varied from 100% DMF to 100% water. As before, the reaction was initiated with the addition of hydrogen peroxide at room temperature and with stirring. Interestingly, and analogous to the dioxane/water system,[1,2] there was no sign of reaction (i.e., no heat or color generation) in the

Table 3. Effect of Solvent Composition on the Polymer Molecular Weight and Dispersity (Reaction in the Absence of Reversed Micelles)

synthesis medium	monomer convn[a] (%)	polymer yield[b] (%)	M_w	M_w/M_n	comments
100/0 DMF/water	0	0			no reaction
85/15 DMF/water	20	10	281	1.23	dimers soluble in 85% DMF
60/40 DMF/water	80	75	612	1.20	oligomers soluble in 60% DMF
40/60 DMF/water	80	80	675	1.05	oligomers soluble in 40% DMF
20/80 DMF/water	75	75	658	1.02	oligomers soluble in 20% DMF
0/100 DMF/water	50	35	400	1.90	oligomers soluble in 100% DMF
85/15 dioxane/water	80	15	3000	2.10	insoluble polymer, soluble oligomers

[a] Monomer converted/monomer added initially. [b] See text for definition.

Table 4. Effect of Solvent Composition on the Polymer Molecular Weight and Dispersity (Reaction in AOT Reversed Micelles)

synthesis medium	monomer convn[a] (%)	polymer yield[b] (%)	M_w	M_w/M_n	comments
100% isooctane	100	100	2500	1.36	$W_0 = 15$
100% isooctane	90	100	2500	1.38	$W_0 = 9$
75/25 isooctane/$CHCl_3$	100	85	1681	1.53	$W_0 = 9$
50/50 isooctane/$CHCl_3$	100	75	3461	1.85	$W_0 = 9$
25/75 isooctane/$CHCl_3$	75	35	3601	1.83	$W_0 = 7$, phase separation
100% $CHCl_3$	20	10	1000	1.07	$W_0 = 7$, phase separation

[a] Monomer converted/monomer added initially. [b] See text for definition.

reaction mixtures containing 85% or more organic solvent, and the solutions remained clear throughout the addition of hydrogen peroxide. On the other hand, heat evolution (due to exothermic reaction[3]) followed the reaction in solvents with 60% or less DMF, and the solutions became colored and opaque instantaneously. It is clear that DMF sustained enzyme activity, although the presence of water was necessary. The monomer solubility in 20% DMF solution was poor, and the solution turned into a stable emulsion prior to initiating the reaction. The reactions were continued for a few more hours before the solvent was evaporated under reduced pressure. The precipitates were washed with water and isooctane to remove buffer salt, the enzyme, and any unreacted monomer. The dried precipitates were dissolved in 1% LiBr/DMF, and their molecular weights were analyzed as described earlier (Table 3).

The polymer yield, defined as a ratio of the amount of polymer recovered as an insoluble fraction in isooctane to the amount of monomer converted, was about 75% for cases where the DMF content in the reaction mixture was between 20% and 60%. Molecular weight analyses revealed that the polymers were in fact oligomers with an average molecular weight of about 650, significantly lower than that obtained with the AOT/isooctane reversed-micellar system, and had a polydispersity of 1.03–1.20. The molecular weight was not variable with the DMF content, indicating that either the solubility of growing chains during the reaction was not sustained by DMF/water (up to 60% DMF) or the enzyme became inactive. Analogous to the dioxane/water system, the monomer conversion was either absent or poor at higher DMF contents, presumably due to significant enzyme inactivation.

In order to minimize the enzyme inactivation, a less polar solvent than DMF was sought as the reaction medium. Accordingly, chloroform was used to carry out the phenol polymerization reaction. A mixture of chloroform and isooctane was used for the reactions, and the polarity of the medium was gradually varied by adding chloroform and thus changing the composition from 100% isooctane to 100% chloroform. However, the enzyme powder was poorly dispersed in this solvent system, and it became necessary to prepare AOT reversed micelles with the chloroform/isooctane mixture, as described earlier. As the isooctane content in the reaction mixture was lowered from 100%, the polymer yield dropped from 100% (in pure isooctane reversed micelles) to about 10% (in pure chloroform reversed micelles) (Table 4).

The polymer molecular weight was maximum at 50–75% chloroform in isooctane with a polydispersity of about 1.8. However, the polymer exhibited a low polydispersity of 1.07 in 100% chloroform. The poor polymer yields at high chloroform contents are perhaps due to the formation of unstable microemulsion systems leading to phase separation. As a result, the contact between the enzyme and the monomer is inefficient and the polymer yield is poor. Smaller W_0 values also contribute to poor monomer conversion.[3] One approach is to eliminate the surfactant altogether by polymerizing phenolic monomers in a biphasic system where a large amount of water containing enzyme is mechanically dispersed in a hydrophobic organic solvent containing the monomer. Preliminary results indicate that a number of polyphenols including poly(*p*-ethylphenol) of molecular weight 2500 can be prepared in a chloroform/buffer (50:50, v/v) biphasic system.

The hydroxyl groups in enzymatically prepared polyphenols do not participate in bond formation, as noted earlier from ^{13}C-NMR studies. The FTIR spectrum of the polymer (Figure 6) also illustrates the point with a broad peak at 3400 cm^{-1} due to O–H stretch. Thus the hydroxyls on the polymer are available for chemical modifications such as esterification. Esterification was carried out in chloroform with palmitoyl and cinnamoyl chlorides in the presence of a stoichiometric amount of pyridine to scavenge HCl produced in the reaction. Parts a and b of Figure 6 illustrate FTIR spectra of poly(*p*-ethylphenol) before and after functionalization with palmitoyl and cinnamoyl moieties, respectively, at the hydroxyl groups of the polymer. The presence of alkyl chains in the polymer due to palmitoyl groups was confirmed by the presence of strong peaks between 2800 and 3000 cm^{-1} due to asymmetric and symmetric C–H stretches in methyl and methylene groups of the alkyl chains (Figure 6a). In addition, the peak for the O–H stretch at 3400 cm^{-1}

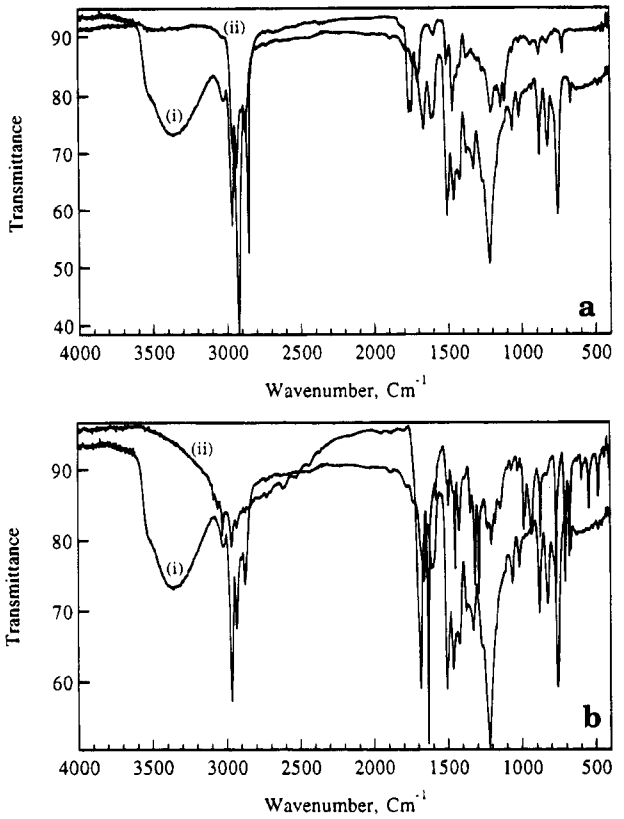

Figure 6. (a) FTIR spectra of poly(*p*-ethylphenol) (i) before and (ii) after esterification with palmitoyl chloride. (b) FTIR spectra of poly(*p*-ethylphenol) (i) before and (ii) after esterification with cinnamoyl chloride.

disappeared in the esterified polymer, indicating the participation of the hydroxyl groups in the reaction. The ester formation was also confirmed by the presence of the C=O stretch at 1750 cm^{-1} in the modified polymer. Similarly, cinnamoylation of the polymer was confirmed by the disappearance of the O–H stretch as well as by the strong presence of the C=C ring stretch at 1600 cm^{-1} (Figure 6b). UV spectroscopic studies, carried out with acetonitrile solutions of the polymer, showed an increased absorbance for the cinnamoylated polymer at 259 nm due to the presence of an additional phenyl ring (Figure 7).

Conclusions

Free-radical polymerization of *p*-ethylphenol, catalyzed by horseradish peroxidase, was carried out at ambient conditions in a number of organic solvent systems. While the AOT/isooctane reversed-micellar system afforded complete monomer conversion into polymer with an average molecular weight of 2500, the addition of chloroform yielded lower molecular weights, with narrower distributions. Reactions carried out in DMF produced mostly oligomers with uniform molecular weights. Analysis of poly(*p*-ethylphenol) by GPC

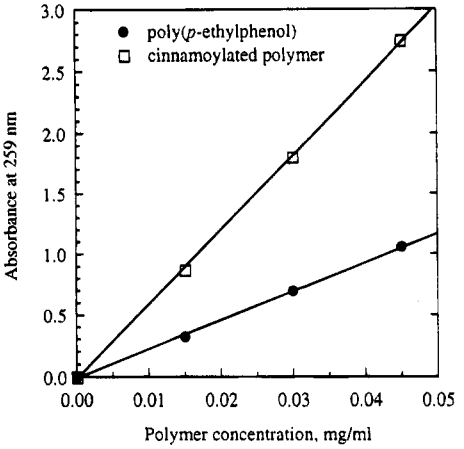

Figure 7. UV absorbance at 259 nm of poly(*p*-ethylphenol) before and after cinnamoylation.

demonstrated the effect of LiBr on the molecular weights of poly(*p*-ethylphenol) and poly(*p*-phenylphenol). The polymers showed apparently high molecular weights in DMF due to significant inter/intramolecular associations. At 0.35% LiBr in DMF and above, these interactions were eliminated to permit the estimation of true molecular weights. ^{13}C-NMR and FTIR studies revealed that the repeat units in the polymer are primarily linked at ortho positions. The hydroxyl groups, which are not involved in bond formation, could be derivatized with palmitoyl and cinnamoyl chlorides.

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