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Enzyme-Mediated Two-Dimensional Polymerization of Aromatic Derivatives on a Langmuir Trough

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An examination of the assembly and biocatalytic polymerization of mixed aromatic monomeric systems was undertaken using the Langmuir–Blodgett technique. Pressure–area isotherms of 4-(tetradecyloxy)phenol, 4-(hexadecyloxy)phenol, 4-(hexadecyl)aniline, 4-ethylphenol, pyrrole, aniline, and phenol in various ratios were determined. Polymerizations on the Langmuir trough were carried out using the enzymes horseradish peroxidase and laccase. UV–vis spectroscopy revealed that the polymerized monolayers possess extensive electronic conjugation in the polymer backbone. Fourier-transformed IR, attenuated total reflection–Fourier-transformed IR, thermal gravimetric analysis, conductivity, and nonlinear optical properties were measured to characterize the monolayers, to determine the extent of conjugation, to assess the orientation of the alkyl chains with respect to the substrate surface for LB films with multilayers, and to assess electrical and optical properties.

Introduction

The Langmuir trough (LT) (Figure 1) is useful in organizing amphiphilic reactants at the air–water interface. These reactants are surface-active substances consisting of both a hydrophilic group at one end and a long hydrophobic tail at the other. The control of the resulting ordered monolayer structure, stereochemistry, and orientation on the LT is improved, thus enabling further refinement of a polymer's functional properties (Gaines, 1966). This 2D lattice, which takes the form of a monomolecular or monolayer film, is transferred from the trough and deposited on an appropriate substrate (Figure 2). Monolayers conforming to this manner are termed Langmuir–Blodgett (LB) films. Polymerization of the assembled surfactant monomers may be achieved by a variety of techniques (Ulman, 1991).

Past experiments involving enzyme-catalyzed oxidative coupling reactions of *p*-phenylphenol and aniline/benzidine compounds have been carried out in bulk, in solvents, and in near water-free organic solvents (Dordick et al., 1987; Akkara et al., 1991). Polymers synthesized in organic solvents had high molecular weights, good thermal stability, and significant third-order nonlinear optical properties. Electrical conductivity of the polymers after doping was also demonstrated. However, branching and cross-linking, originated by the ortho–para directionality of the monomers, were present, based on limited solubility in organic solvents, differential scanning calorimetry (DSC), NMR, and Fourier-transformed IR (FTIR), creating solubility as well as processing problems and nonoptimized configurations for electrical and optical performance.

The objective of the present investigation was to use a LT for the enzymatic polymerization of a suitably ordered and oriented monomer to achieve an ordered

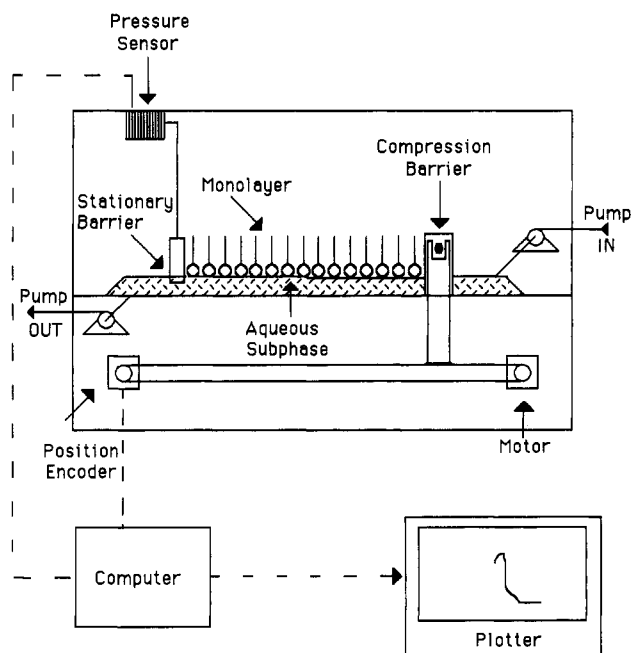


Figure 1. Schematic view of a conventional Langmuir trough.

lattice. This approach was believed to be capable of improving the electronic and nonlinear optical properties, and processability, of the highly ordered polymeric products (Tieke et al., 1981).

The experimental approach required the synthesis of novel phenolic surfactant molecules. Here we describe the synthesis and characterization of 4-(hexadecyloxy)phenol (C16PP) and 4-(tetradecyloxy)phenol (C14PP). Pressure–area isotherms of C16PP, C14PP, 4-hexadecylaniline (C16PA), 4-ethylphenol (C2PP), pyrrole, aniline, and phenol (Figure 3) in various ratios on buffered MilliQ water (pH 7.5) with and without the enzyme horseradish peroxidase (HRP) are reported. Hydrogen peroxide was the electron acceptor in the reactions. Furthermore, spectroscopic, thermal, and electrooptical measurements are also reported for the polymer products.

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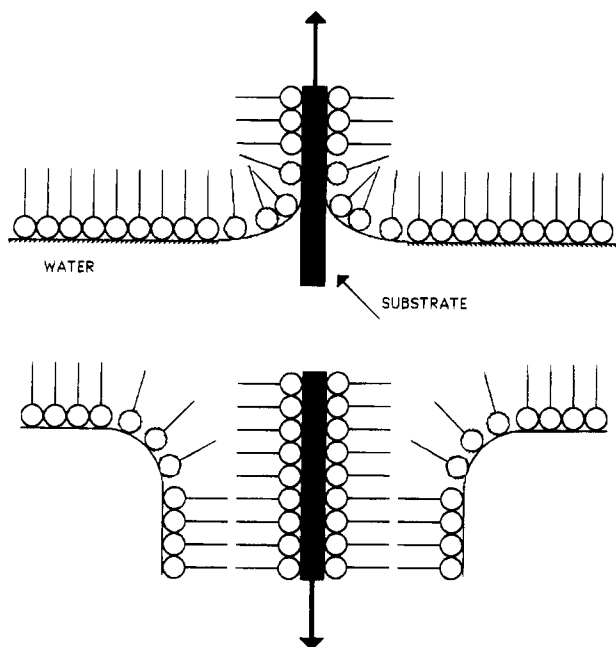


Figure 2. Dipping procedure for the formation of LB films.

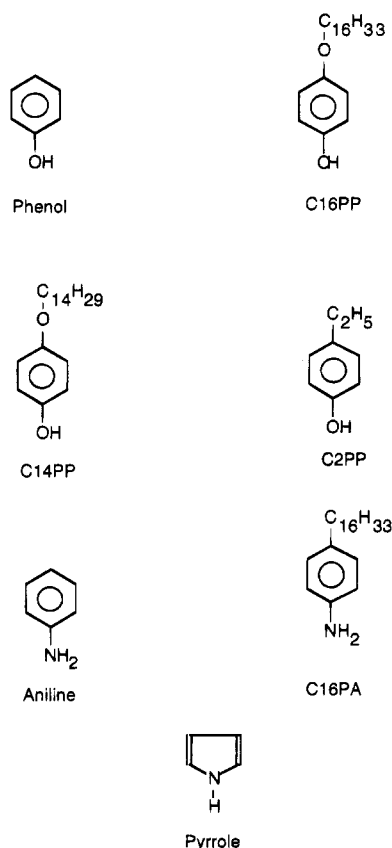
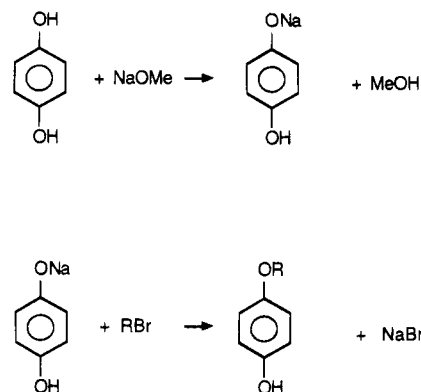


Figure 3. Monomers utilized for this work.

Experimental Section

All chemical reagents were purchased from Aldrich Chemical Co. (Milwaukee, WI) and were used as received. The enzymes HRP (EC 1.11.1.7 Type II, 150–200 units/mg), laccase (LAC) (benzenediol:oxygen oxidoreductase, EC 1.10.3.2, 120–150 units/mg), and the buffer (*N*-(2-hydroxyethyl)piperazine-*N'*-2-ethanesulfonic acid, HEPES) were purchased from Sigma Chemical Co. (St. Louis, MO). C16PA, C2PP, pyrrole, phenol, hydrogen peroxide, dimethyl sulfoxide (DMSO), and aniline were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received.



R for C16PP is C₁₆H₃₃- and for C14PP, R is C₁₄H₂₉-

Figure 4. Scheme of the synthesis of C16PP and C14PP.

The monomers and the polymers were characterized by FTIR (PE1760X, Perkin-Elmer, Norwalk, CT), ¹H NMR (VXR-400; Varian, Palo Alto, CA), Perkin-Elmer (Perkin-Elmer, Norwalk CT) Lambda-9 UV-vis-near-IR spectrophotometry, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) (DSC3910; TA Instrument, New Castle, DE), and elemental analysis (Atlantic Microlab Inc., Norcross, GA).

For the synthesis of C16PP (see Figure 4), we used the following procedure: To a methanolic solution (50 mL) of hydroquinone (2.2013 g, 20.01 mmol) was added dropwise NaOMe (1.0816 g, 20.02 mmol) in 50 mL of methanol, and the resulting solution was stirred for 10 min. After the addition of 10 mL of dry toluene the solvents were evaporated to dryness under reduced pressure. The solid residue was cooled to room temperature, and 1-bromohexadecane (6.1065 g, 20.00 mmol) in 25 mL of freshly distilled dimethylformamide (DMF) was added. The resulting mixture was stirred for 2 h at 110 °C under nitrogen. The brown solution was then cooled and poured into 500 mL of cold water. The product was filtered and dried at room temperature under vacuum. The C16PP compound was purified by column chromatography (silica gel, with toluene/diethyl ether (9:1) as eluent) as a white solid which on crystallization from benzene formed white needles. In a similar way C14PP was synthesized with 1-bromotetradecane (5.5502 g, 20.02 mmol) in place of 1-bromohexadecane.

A commercial Lauda film trough (Langmuir Filmwaage, Model D; Lauda-Brinkman, Westbury, NY) equipped with a constant-temperature bath was utilized. Monomers at 1–2 mg/mL concentration were solubilized in chloroform and spread at the air–water interface (Bruno et al., 1991). The subphase contained 2 L of 0.85 mM HEPES buffer, pH 7.5, with 12–25 mg of enzyme/L. Once the monomer at the air–water interface was spread onto the aqueous subphase including HRP and compressed to 15 mN/m, 0.300 mL of hydrogen peroxide (3% in volume) was injected into the subphase to initiate the polymerization. All the polymerizations involving aniline were conducted in darkness.

The progress of the reactions on the trough could be visually followed by slight color changes within the first few minutes. Reactions were concluded after 8 h. At this point the subphase composition was changed by using a pump to replace the subphase with fresh ultrahigh-purity water. The resultant two-dimensional polymer networks were transferred onto various substrates for characterization. For UV-vis spectroscopy,

the polymer monolayers were transferred onto quartz slides. The polymer also was collected on the surface of the trough, dried, and dissolved in DMSO. The solution was transferred into quartz cells for UV measurements. Spectral characterization was performed with a Perkin-Elmer Lambda-9 UV-vis-near-IR spectrophotometer (Norwalk, CT). Spectral characterizations of monolayers and polymers on ZnSe slides and on KBr plates, respectively, were performed with a Perkin-Elmer 1760 FTIR-FTRaman spectrophotometer (Norwalk, CT). TGA (TA Instrument, New Castle, DE) was conducted under a nitrogen atmosphere, and the temperature rise was 10 °C/min. For electrical measurements, an Interdigitated Microsensor Electrode (IME) was used. The IME was composed of 50 gold fingers, each 15 μm wide, 4985 μm long, and with a space of 15 μm between each finger. These sensors were covered with bulk polymer and then placed in a sealed chamber where nitrogen was alternatively flushed and vacuumed three times, followed by measurement of the resistance of the undoped polymer. Nitrogen was gradually introduced along with dopant (iodine) into the chamber, and the electrical resistance was monitored. The measurement was halted when saturation in conductivity resulted.

Third-order nonlinear optical (NLO) properties ($\chi^{(3)}$) were determined in solution by degenerate four-wave mixing with a frequency-doubled Nd:YAG laser at 532 nm with 17 ps pulses. The average energy per pulse was 25 mJ. The vertically polarized output was split into three beams, which are temporally and spatially overlapped in the sample contained in a 1 or 2 mm cuvette (Fisher et al., 1992).

An alternate method of enzymatic polymer synthesis from mixtures of substituted C14PP and phenol monomer (in the ratio 1:10) involved the injection of 2 mL of a LAC solution (10 mg/mL) into the buffered (pH 7.5) subphase (no hydrogen peroxide was required for this polymerization). The surfactant was compressed at the rate of 1.0 $\text{\AA}^2 \text{mol}^{-1} \text{min}^{-1}$ to a surface pressure of 15 mN/m followed by enzymatic polymerization for 15 h at 20 °C prior to deposition.

For the HRP-mediated polymerization an injection of hydrogen peroxide ($4.27 \times 10^{-5} \text{ M}$) was made into the subphase at 37 °C of mixed C16PP and phenol monomers (ratio 1:10). It was not possible to detect any polymer formation from the same mixture at 20 °C.

Results and Discussion

The yield of the monomer C14PP during the synthesis was 0.6 g (10.0%), and the melting point was 87 °C (Figure 5B). The FTIR (Figure 5A) of the C14PP KBr disk showed a 3439 cm^{-1} peak indicative of OH stretching, a 1512 cm^{-1} peak indicative of a C=C ring stretch, and a 1251 cm^{-1} peak indicative of COC stretching. The NMR (Figure 5C) measured the expected shifts for the OH proton at 8.3540 ppm and for the CH_3 protons at 0.3587 ppm. The elemental analysis indicated the following ratios for the monomer synthesized: C = 76.98% (calculated C = 78.43%) and for H = 10.76% (calculated H = 11.11%).

The yield of monomer C16PP was 0.7 g (10.5%), and the melting point was 91 °C (Figure 6B). The FTIR (Figure 6A) of C16PP in a KBr disk showed a 3457 cm^{-1} peak indicative of OH stretching, a 1511 cm^{-1} peak indicative of a C=C ring stretch, and a 1250 cm^{-1} peak indicative of COC stretching. The NMR (Figure 6C) measured the expected shifts for the OH proton at 8.3518 ppm and for the CH_3 protons at 0.3580 ppm. The

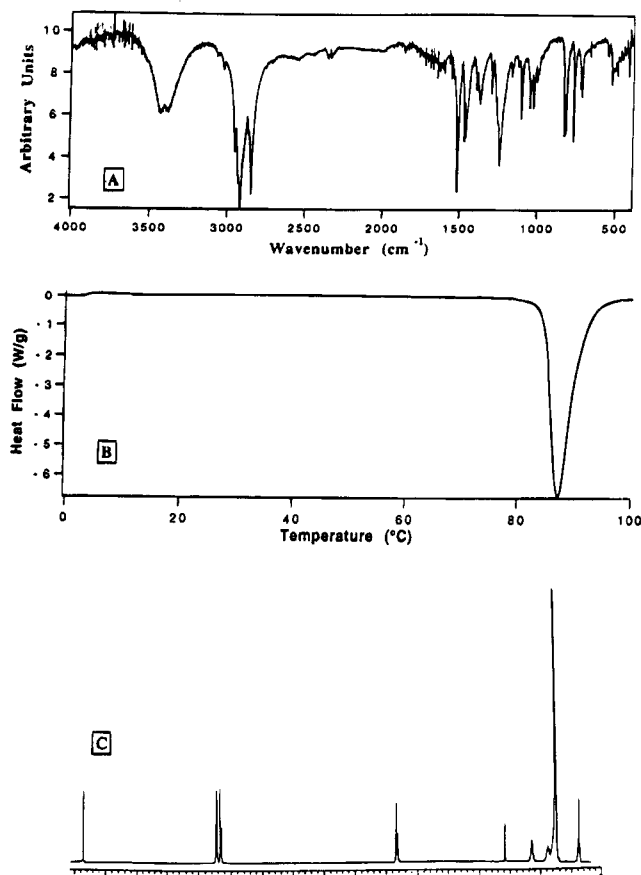


Figure 5. FTIR (A), DSC (B), and NMR (C) of C14PP.

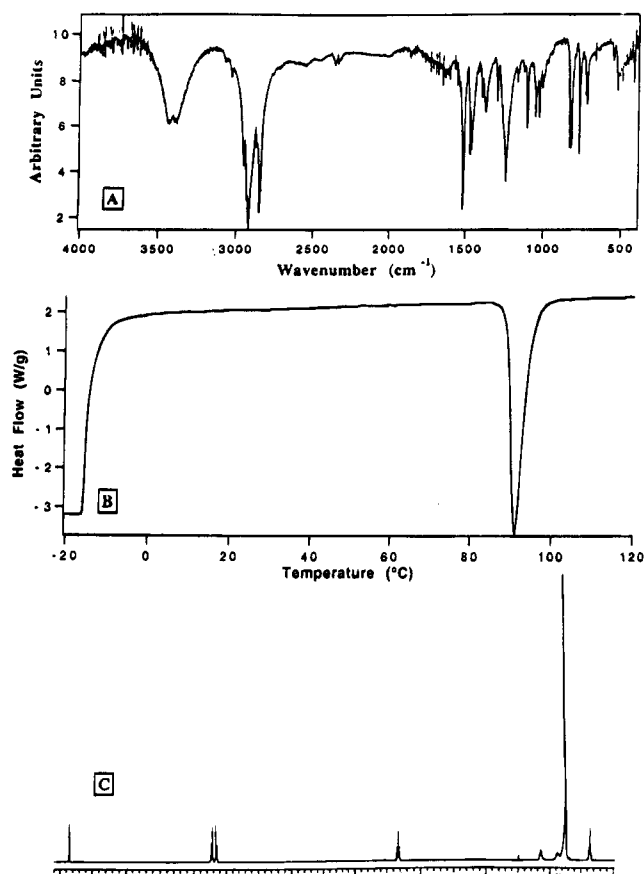


Figure 6. FTIR (A), DSC (B), and NMR (C) of C16PP.

elemental analysis indicated the following ratios for the monomer synthesized: C = 78.04% (calculated C = 79.04%) and H = 10.97% (calculated H = 11.37%).

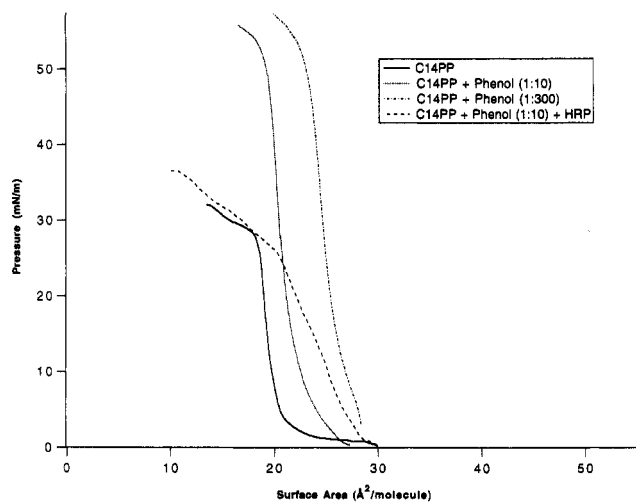


Figure 7. Isotherms of C14PP and phenol on buffered MilliQ water and in the presence of HRP.

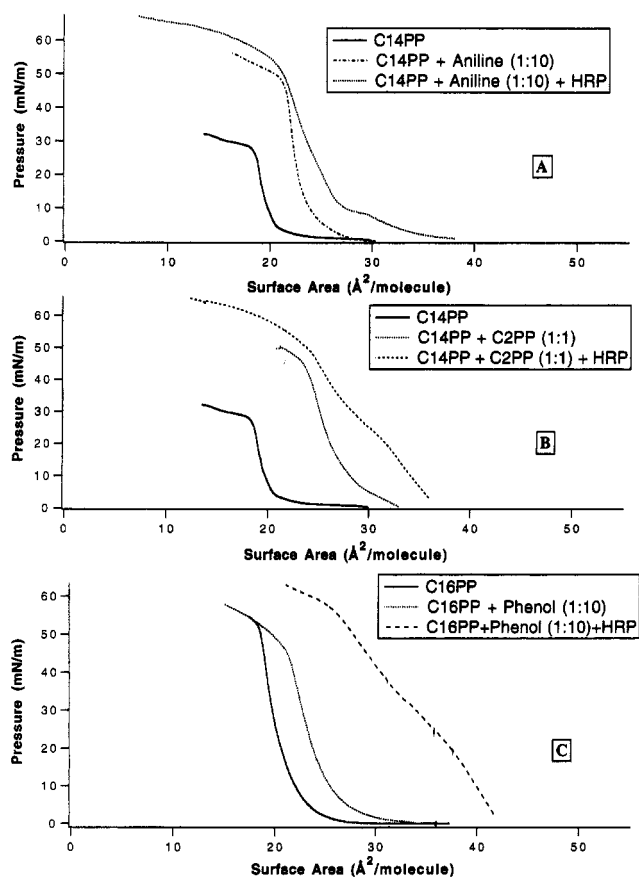


Figure 8. Isotherms of C14PP/aniline (A), C14PP/C2PP (B), and C16PP/phenol (C) on buffered MilliQ water and in the presence of HRP.

Pressure–area isotherms with unreacted monomers C14PP and C16PA and mixtures of these monomers with phenol and aniline are shown in Figures 7–9. Approximately 22–25 Å²/molecule was observed for the pure monomer system. This increased area per molecule in comparison to the area per molecule of an alkyl chain (20 Å²/molecule (Gaines, 1966)) may be attributed to the presence of the phenol group. It is interesting to note that the introduction of the phenoxy, aniline, or pyrrole group into the interior of the monolayer does not disturb the stability of the close-packed monolayer, as shown by the isotherm of the derivatized monomers reaching relatively high collapsed pressure values of about 40–70 mN/m.

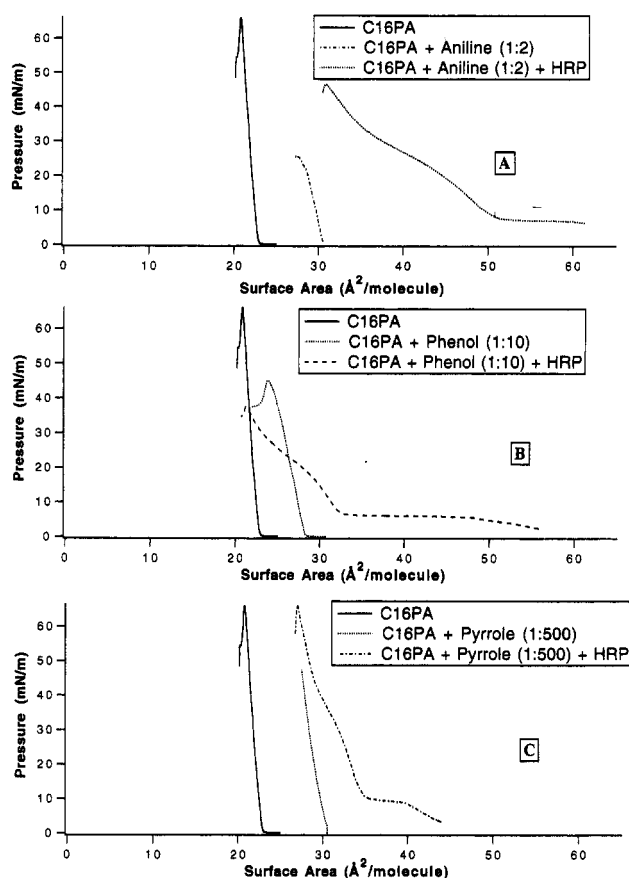


Figure 9. Pressure–area isotherms of C16PA/aniline (A), C16PA/phenol (B), and C16PA/pyrrole (C) on MilliQ water and in the presence of HRP.

The expansion in pressure–area isotherms with added enzyme and underivatized monomers may be due to the permeation of the monolayer and interaction of enzymes with monomers.

Underivatized phenol, aniline, or pyrrole was added to the trough in ratios ranging from 1:1 to 500:1 (underivatized/derivatized). The reaction rate, upon injection of hydrogen peroxide, was observed to increase as the ratio increased. Following the 8 h reaction, we were able to completely compress the film with the movable barrier and collect the polymer which was an easily extendable, fiberlike material (Bruno et al., 1991). UV–vis spectroscopic characterizations (Figures 10–13) of the HRP polymerized mixture of underivatized/derivatized monomers exhibited broad absorption in the visible spectrum, indicative of the formation of a conjugated polymeric backbone structure. This absorption feature was absent in controls containing only the monomer mixtures. Controls run in the absence of either hydrogen peroxide or HRP also gave no evidence of polymer formation.

Similar results were obtained for the C14PP/phenol reaction mediated by LAC. An extensive absorption was found in the UV–vis spectra (Figure 12C) signifying a presence of a large conjugation in the polymeric backbone.

In contrast to the LB polymerization of the C14PP/phenol system at 20 °C reported earlier (Bruno et al., 1991), no reaction was observed at 20 °C for the C16PP/phenol system, but a reaction occurred at 37 °C. This difference may be attributed to an Arrhenius effect, or different phase behavior.

We did not observe, at temperatures up to 40 °C, any reaction for a C16PA/pyrrole mixture (ratio 1:500),

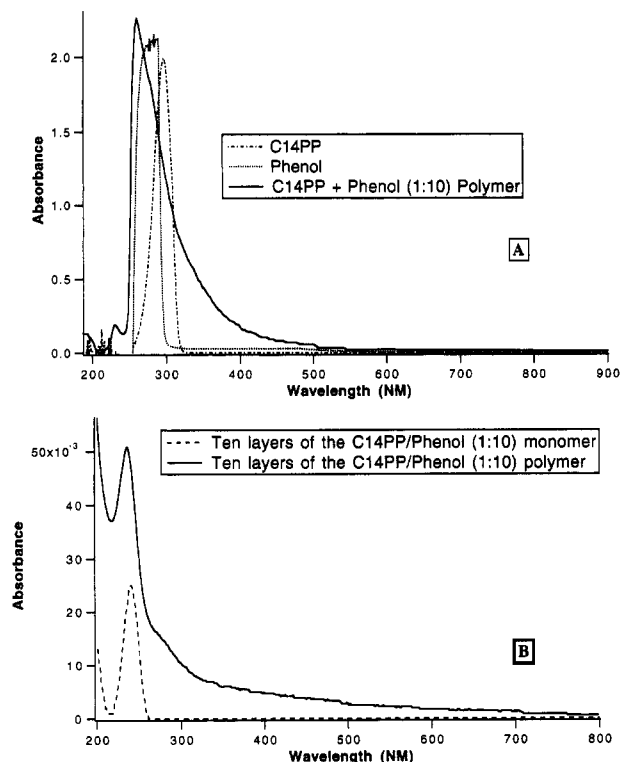


Figure 10. UV-vis spectra of C14PP in monomer form and in polymer form with phenol collected on the LT surface (A) and deposited on the quartz slide (B).

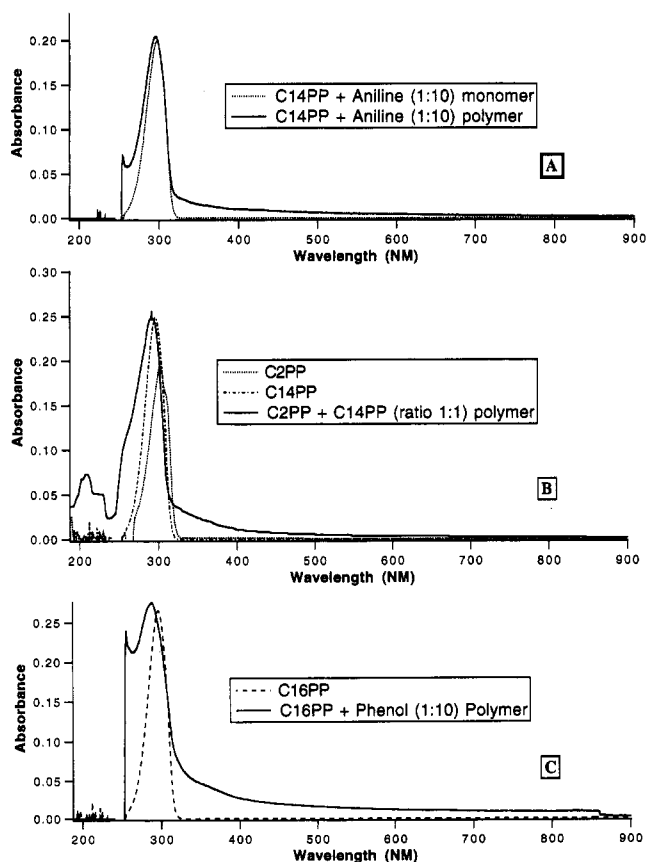


Figure 11. UV-vis spectra for a DMSO solution of C14PP/aniline (A), C14PP/C2PP (B), and C16PP/phenol (C) monomer and polymer.

indicating that not all aromatic monomers can serve as substituents for these reactions to generate free radicals.

Spectroscopic characterization was also carried out by FTIR and attenuated total reflection-Fourier-trans-

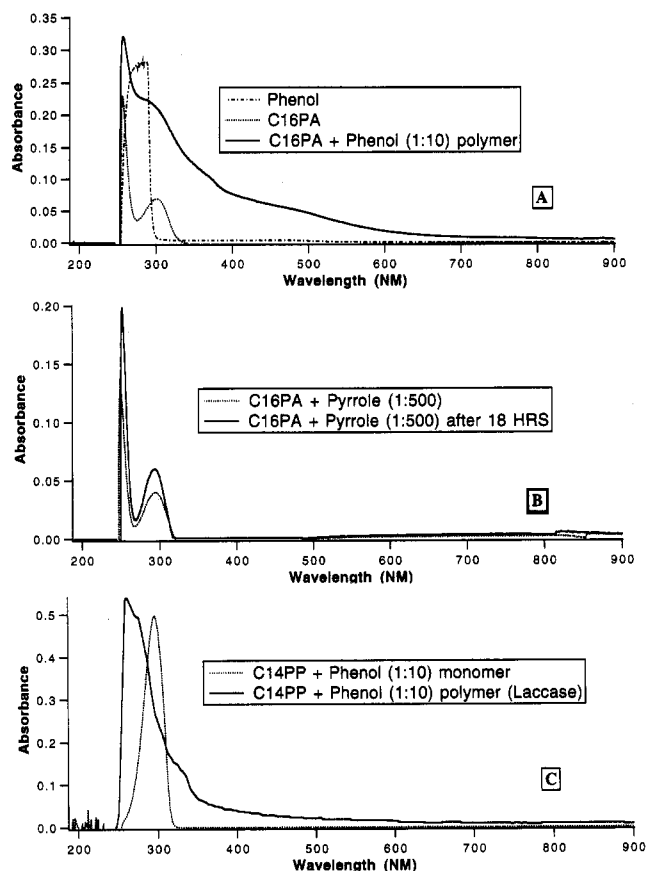


Figure 12. UV-vis spectra for a DMSO solution of C16PA/phenol (A), C16PA/pyrrole (B), and C14PP/phenol (laccase enzyme) (C) monomer and polymer.

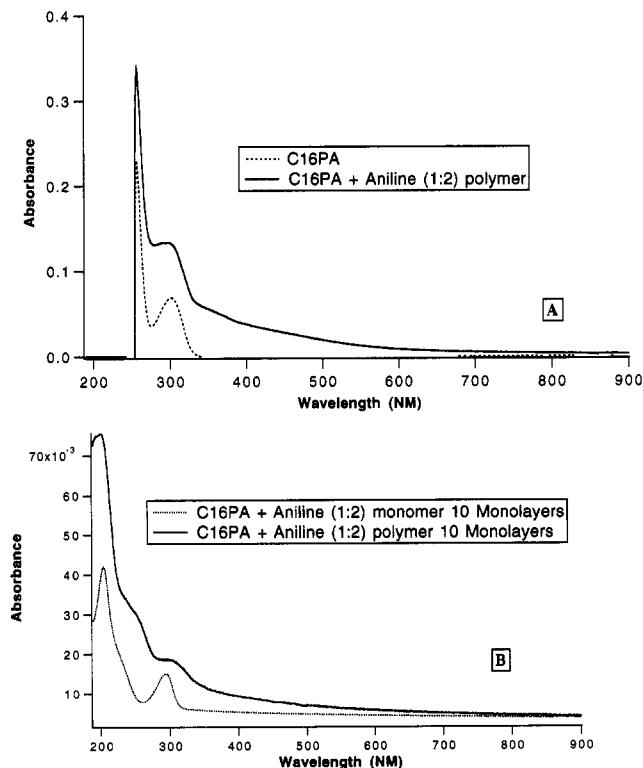


Figure 13. UV-vis spectra of C16PA in monomer form and in polymer form with aniline collected on the LT surface (A) and deposited on the quartz slide (B).

formed IR (FTIR-ATR) (Figures 14 and 15). The polymer and the monomer in bulk and as monolayers form were deposited on KBr wafers and ZnSe slides, respectively. The FTIR-ATR of the C14PP/phenol

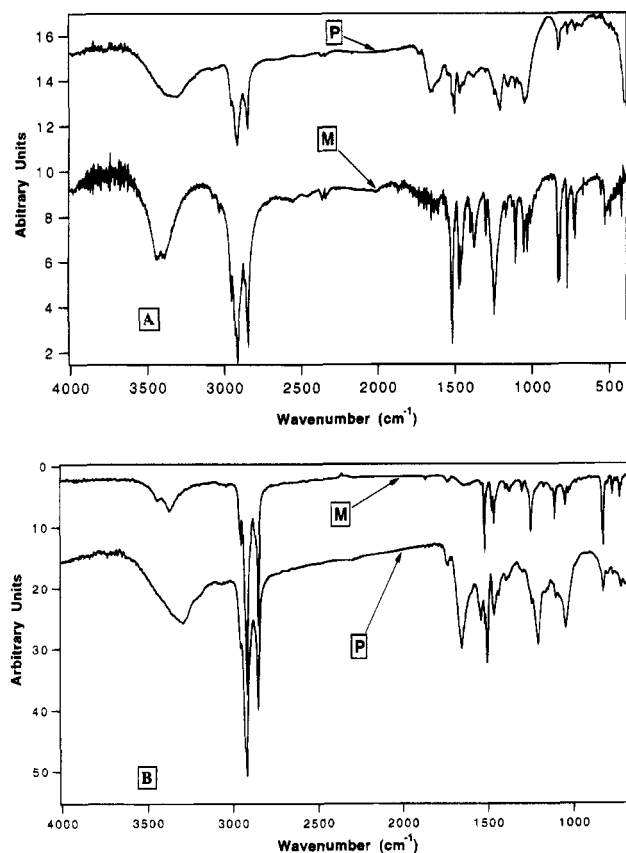


Figure 14. FTIR spectra of C14PP in monomer form and in polymer form with phenol collected on the LT surface (A) and FTIR-ATR spectra of the monomer/polymer deposited on the ZnSe slide (B).

polymer shows changes in the regions 1600–1700 and 3500–3300 cm^{-1} . The broadened peak in the 1600–1700 cm^{-1} region indicates a C=O bond attached to a delocalized conjugated backbone. The broadened intense peak at 3500 cm^{-1} shows the changed nature of the hydrogen bonding of the OH groups due to polymerization. A large conjugation band (1560–1710 cm^{-1}) is also present in the polymer formed by the mixture C16PA/aniline (ratio 1:2) (Figure 15). It is important to note that peak widths for all bands are narrow from the monolayer polymer (Figures 14b and 15b) compared to the polymer skimmed from the top of the LT (Figures 14a and 15a) with a value of 10–30 cm^{-1} , indicating a possible orientation in the polymeric thin layer compared to the bulk polymer.

Thermal properties of the polymers were determined by TGA, and thermograms of C14PP/phenol (ratio 1:10) and C16PA/aniline (ratio 1:2) are illustrated in Figure 16. The TGA analysis indicated that a significant amount of material remains after heating the polymer to 900 °C in a N_2 atmosphere. TGA of the C14PP/phenol polymer had two major transitions, one between 250 and 400 °C and the other between 400 and 470 °C. Thermal analysis of the C16PA/aniline polymer showed 50% of the final residue and similarly the presence of two different transitions during the degradation process. The chemical and physical properties of this residual material have not been studied.

Conductivity of iodine-doped polymerized multilayers of C16PA and aniline ranged from 3×10^{-3} to 1×10^{-5} S/cm, the semiconductive range. The polymer assembled from the mixture C16PA and aniline (1:2) was relatively stable and maintained a conductivity of 2×10^{-4} S/cm over a 3 day period after doping. The C14PP/

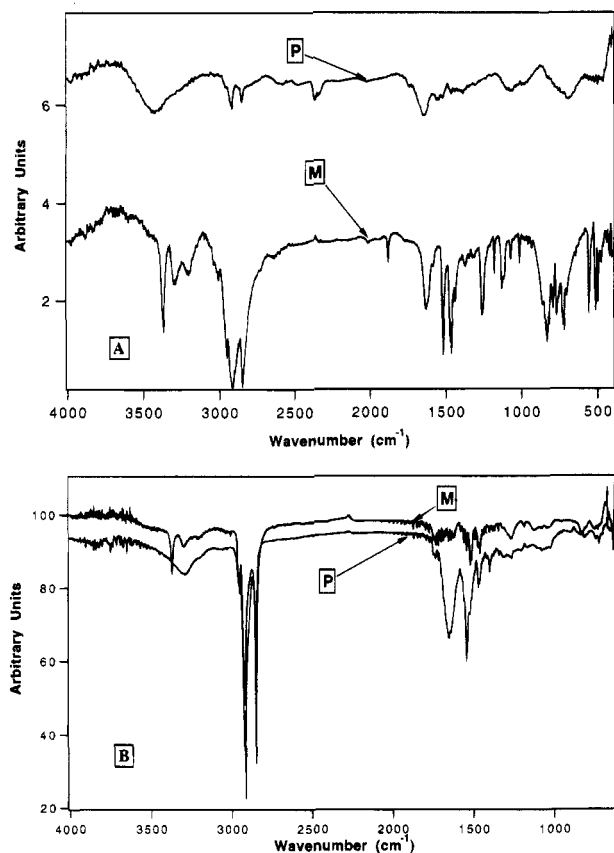


Figure 15. FTIR spectra of C16PA in monomer form and in polymer form with aniline collected on the LT surface (A) and FTIR-ATR spectra of the monomer/polymer deposited on the ZnSe slide (B).

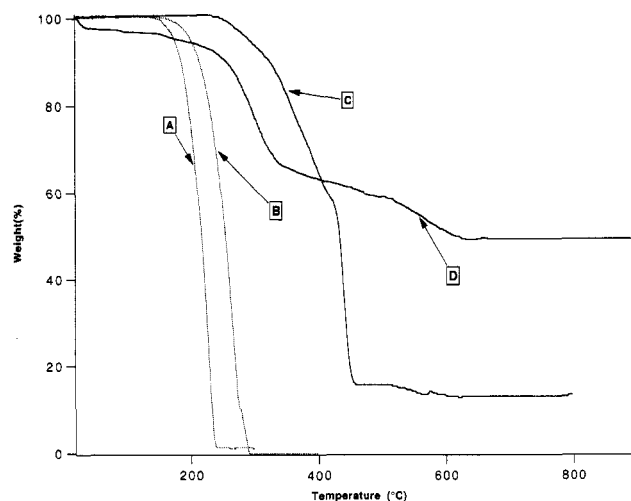


Figure 16. TGA of monomers C14PP (A) and C16PA (B) and of polymers formed by the mixtures C14PP/phenol (C) and C16PA/aniline (D).

phenol polymer showed similar behavior (Bruno et al., 1994) although the initial conductivity was higher.

There was a 1 order of magnitude increase in the third-order optical nonlinearities to values of 1×10^{-9} esu upon polymerization of the C14PP/phenol system compared to polymers synthesized in bulk solvents (Table 1).

A schematic of two possible arrangements of the polymerization products is given in Figure 17. It is believed that the structure in Figure 17B is most likely the dominant structure for the system C14PP/phenol. The orientation of the alkyl chain was calculated according to established procedures (Haller et al., 1970).

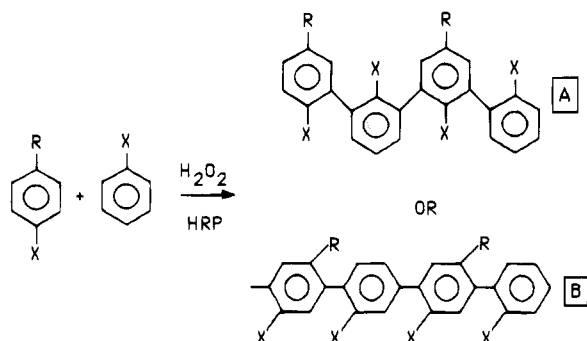


Figure 17. Schematic of the polymerization process at the air-water interface.

Table 1. NLO Data for Different Phenolic Polymers

polymer/system type	refs	$\chi^{(3)}$ ($\times 10^{-10}$, esu)
poly(ethylphenol)		
in isooctane	Ayyagari (1992)	0.68
in dioxane/water	Ayyagari (1992)	0.68
poly(dodecylphenol)		
in isooctane reversed micelle	Akkara et al. (1994)	0.47
in isooctane/water system	Akkara et al. (1994)	0.54
C14PP/phenol (1:10)		
Langmuir-Blodgett		10.0
C16PA/phenol (1:10)		
Langmuir-Blodgett		10.1

These conclusions, reported by our group in a previous paper (Bruno et al., 1995), are based on spectroscopic measurements and modeling calculations (Bruno et al., 1994). A homopolymerization of C14PP or of the phenol at the air-water interface is not predicted. C14PP by itself does not homopolymerize because of steric hindrance caused by the presence of the alkyl chain. Furthermore, the phenol does not form a monolayer on the LT and, consequently, homopolymers of phenol at the air-water interface are not possible. The FTIR of the final monolayer showed a C14PP/phenol ratio of 1:2. In this work we do not claim the presence of a perfect alternating copolymer. For C16PA/aniline an ortho-ortho directionality (Figure 17b) is envisioned based on spectroscopic measurements.

Conclusions

This work concerns a novel approach for the synthesis of polymers by enzyme catalysis *in situ* using a Langmuir trough. The LT is used to orient and order the monomers prior to the enzyme-based polymerization. Using this approach, polymer properties may be improved for increased heat stability, nonlinear optical response, and electrical conductivity.

The approach to the 2D polymer network synthesis described here is an enzyme-mediated free-radical polymerization process. In the present work, a wide range of monomers was found to react under these conditions which provides a diversity of potential polymer products for systematic studies of the effect of monomer substituents on mechanical, thermal, electronic, and optical properties. The process described represents a general technique for the assembly and polymerization of semiconductive and optically active polymers in 2D networks. Processing limitations with intractable polymers synthesized in bulk are overcome, and thin films are formed as the reaction progresses.

Acknowledgment

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Nomenclature

C16PP = 4-(hexadecyloxy)phenol

C14PP = 4-(tetradecyloxy)phenol

C16PA = 4-hexadecylaniline

C2PP = 4-ethylphenol

FTIR-ATR = Fourier-transformed IR-attenuated total reflection

DSC = differential scanning calorimetry

FTIR = Fourier-transformed IR

IME = interdigitated microsensor electrodes

LAC = laccase

LB = Langmuir-Blodgett

LT = Langmuir trough

HEPES = *N*-(2-hydroxyethyl)piperazine-*N'*-2-ethanesulfonic acid

NLO = nonlinear optical

TGA = thermogravimetric analysis

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