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OFFICE OF NAVAL RESEARCH
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R&T Code 4132058---02

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TECHNICAL REPORT NO. 11

Electrochemically Mediated Polymerization of 2-Pentadecylaniline
Confined to a Planar Liquid-Liquid Interface

by

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1. AGENCY USE ONLY (Leave blank) 2. REPORT DATE 10/20/93 3. REPORT TYPE AND DATES COVERED Technical

4. TITLE AND SUBTITLE
Electrochemically Mediated Polymerization of 2-Pentadecylaniline Confined to a Planar Liquid-Liquid Interface

5. FUNDING NUMBERS
N00014-91-J-1655

6. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NUMBER
11

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10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
submitted to "Die Makromolekulare Chemie"

12a. DISTRIBUTION / AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
Spreading, isotherms, and polymerization of 2-pentadecylaniline at a planar aqueous electrolyte-organic interface were examined by monitoring the interfacial pressure employing the Wilhelmy-plate method. These results indicate the presence of monomer confined to the interface. Application of a voltage across the interface using stainless steel electrodes results in polymerization to form an electroactive polymer. The interfacial polymerization appears to be affected by metal ions formed by oxidation of the anode that have diffused into the aqueous electrolyte. This phenomenon is dependent on the nature of the electrode material as successful polymerization was not observed with other electrode materials. The polymer formed was soluble in polar organic liquids, was green in its reduced state, and blue in its oxidized state when oxidized and reduced chemically or electrochemically as a thin film. Cyclic voltammetry of the polymer indicates one reversible redox process suggesting that there are only two different oxidation states available, i.e., the equivalent to leucomeraldine cannot be formed with poly(2-pentadecylaniline) in a thin film. However, the fully reduced yellow leucomeraldine can be formed in chloroform solution by hydrazine reduction.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT



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Dear Dr. Wegner:

Enclosed is a manuscript (two copies) entitled "Electrochemically Mediated Polymerization of 2-Pentadecylaniline Confined to a Planar Liquid-Liquid Interface" by W. M. Sigmund, A. D. Child, J. R. Reynolds and R. S. Duran to be considered for publication in *Die Makromolekulare Chemie*.

If further information is needed, please let us know.

Sincerely,

A handwritten signature in cursive script that reads "R. S. Duran".

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Enclosure

Submitted to "Die Makromolekulare Chemie"

Electrochemically Mediated Polymerization of 2-Pentadecylaniline Confined to a Planar Liquid-Liquid Interface

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Abstract

Spreading, isotherms, and polymerization of 2-pentadecylaniline at a planar aqueous electrolyte-organic interface were examined by monitoring the interfacial pressure employing the Wilhelmy-plate method. These results indicate the presence of monomer confined to the interface. Application of a voltage across the interface using stainless steel electrodes results in polymerization to form an electroactive polymer. The interfacial polymerization appears to be effected by metal ions formed by oxidation of the anode that have diffused into the aqueous electrolyte. This phenomenon is dependent on the nature of the electrode material as successful polymerization was not observed with other electrode materials. The polymer formed was soluble in polar organic liquids, was green in its reduced state, and blue in its oxidized state when oxidized and reduced chemically or electrochemically as a thin film. Cyclic voltammetry of the polymer indicates one reversible redox process suggesting that there are only

two different oxidation states available, i.e., the equivalent to leucoemeraldine cannot be formed with poly(2-pentadecylaniline) in a thin film. However, the fully reduced yellow leucoemeraldine can be formed in chloroform solution by hydrazine reduction.

Introduction

Synthetic polymer chemistry generally deals with reactions in isotropic solutions, or in bulk, thus giving equal probability of a reaction occurring randomly in any of the three dimensions. This, of course, usually allows side reactions to take place simultaneously with the primary reaction and reduces the configurational order of the products. Nature shows that chemistry can be more specific when reactions are orientally or positionally confined by highly ordered species, such as enzymes¹ or self assembled ordering of molecules in two dimensions at interfaces.² Due to the ordering, the reaction mechanisms may change, leading to compounds with high stereo- and regio-chemical order.³

At a free interface, molecular motion can be limited to a lateral plane allowing considerable control of reactivity. This has been previously shown by our group⁴ with polymerization at planar air-liquid interfaces. By confining this polymerization reaction to the air-liquid interface, it is possible to yield polymer which is soluble in organic solvents with well-defined structure and defined molecular weight.^{5,6,7,8} Recently we have demonstrated controlled polymerization at a second type of free interface that can be manipulated easily: the planar liquid-liquid interface.⁹ We have

observed the chemical polymerization of 2-pentadecylaniline at a planar aqueous-organic interface.

In this work we describe the electrochemically induced polymerization of 2-pentadecylaniline at a planar liquid-liquid interface and the characterization of the polymer formed by cyclic voltammetry and spectroelectrochemistry. Our observation indicates that the polymerization occurs by initial oxidation of certain metals, forming reactive metal ions, which induce polymerization by diffusing to the interface.

Experimental

Chemicals

The monomer, 2-pentadecylaniline, was synthesized using a procedure described previously.¹⁰ The purity of the compound was verified by elemental analysis and NMR. HPLC-grade cyclohexane (Fisher) was used without further purification. Subphase solutions were made with A.C.S. reagent grade sulfuric acid and Milli-Q® water. Electrode materials (platinum, iron, zinc, cobalt, vanadium, nickel, chromium and silver) were 99.9 % bulk-purity (Aldrich) and used as received after cleaning. The surfaces of the electrodes may differ in that higher concentrations of oxides, hydroxides or nitrides are expected. The surface of the stainless steel electrode was characterized by ESCA and consisted of a mixture of iron (93.9 atom percentage), carbon (3.7 atom percentage) and zinc (0.13 atom percentage). The amount of oxygen was 2.3 atom percentage.

Electrochemically Induced Interfacial Polymerization

The experimental setup for the electrochemical interfacial polymerization is shown in Figure 1 A. All experiments were carried out in Pyrex crystallizing dishes, ensuring high purity and allowing the interface to be visibly observable at all times during the reaction. The crystallizing dishes were sequentially cleaned with chromic sulfuric acid, chloroform and hot Milli-Q[®] water before use. The electrode materials were washed with chloroform then flamed with a Bunsen burner and flushed with Milli-Q[®] water before they were introduced into the interface. The electrodes were introduced through the cyclohexane upper layer until they contacted the interface where the aqueous subphase formed a meniscus on hydrophilic electrodes. They were subsequently raised to the point that the edge of the electrode contacted the interface only (see Figure 1 B).

FIGURE 1

The interface was checked for purity by suction of the liquid phases at their interface and concurrent monitoring of the interfacial pressure. When no interfacial pressure change occurred after suction, except that due to displacement of the Wilhelmy plate in the aqueous phase, the system was considered as pure. After checking the cleanliness of the interface, monomer was introduced by injecting a solution of 5×10^{-4} M of 2-pentadecylaniline in cyclohexane into the interface using a gas tight Hamilton syringe. The syringe needle was raised slightly to form a meniscus prior to monomer injection (Fig. 1b). For each experiment 80 ml cyclohexane and 80 ml aqueous

sulfuric acid was used with an interfacial area of 70 cm². The interfacial pressure was monitored using a hydrophilic platinum plate applying the Wilhelmy method with on-line data acquisition through a modified KSV 5000 instrument.¹¹

The interfacial polymerization was studied by varying the electrode materials, the position of the electrodes, the amount spread (i.e., the corresponding theoretical mean molecular area), subphase sulfuric acid concentrations from 0.1 to 4.0 M and the applied potential with a potentiostat.

Electrochemically induced polymerizations were carried out at constant potential using a Princeton Applied Research Model 273 Potentiostat/Galvanostat and a two electrode setup with a platinum cathode. The polymerization reaction was monitored by observation of the interfacial pressure. The polymer was collected by suction removal of the cyclohexane overlayer and the acid subphase, without disturbing the interface-layer, until there was only a small volume of both left. Clean water was then injected into the subphase to wash the polymer and most of the subphase suctioned again. This was repeated twice. After a few hours the residual cyclohexane was evaporated and the polymer was collected by suction through a fine fritted glass disk. Since the polymer is slightly less soluble in cyclohexane it is enriched at the interface, allowing the monomer to be relatively well separated from the polymer; although GPC always showed a small peak for residual monomer.

Thin films of poly(2-pentadecylaniline) were solution cast from chloroform onto indium tin oxide coated glass slides (ITO) with a surface resistance of 40 Ω/cm^2 obtained from Delta Technologies.

Cyclic voltammetry was performed using a Princeton Applied Research model 273 potentiostat/galvanostat. The counter electrode was a platinum flag and a silver wire was used as a quasi-reference electrode. Two electrolytes were investigated: 0.1 M tetrabutylammonium perchlorate (Eastman Chemical) in acetonitrile that was distilled over P_2O_5 , and 1.0 M sulfuric acid.

In situ electrochemical optical measurements were performed on a Varian Instruments Cary 5E UV-VIS-NIR spectrophotometer. The cuvette was fitted with a silver wire quasi reference electrode and a platinum flag counter electrode with a 0.5 cm diameter hole provided for a light path. Spectra were obtained on the polymer film, held at its fully reduced potential, from 280 nm to 900 nm. The potential at the electrode was then stepped in 50 mV intervals and the spectrum recorded after the current decayed to its background value.

Gel permeation chromatography (GPC) results were collected using a Waters Associates liquid chromatograph apparatus equipped with a U6K injector and UV spectrophotometric detector from Perkin Elmer. Two phenomenex 7.8 mm * 30 cm Phenogel 5 consecutive linear gel columns were used, a 500 Å followed by a 1000 Å type. The eluting solvent was HPLC-grade THF at a flow rate of 1.0 ml/min. Retention times were calibrated using polystyrene standards.

Results and Discussion

We have previously demonstrated that it is possible to restrict 2-pentadecylaniline at the planar liquid-liquid interface and polymerize it via an oxidant added to the subphase.⁹ Motivated by

the well-known ability of aniline and its substituted derivatives to polymerize electrochemically,^{12,13} and the fact that interfacial non-monolayer polymerization of pyrrole can be carried out both chemically¹⁴ and electrochemically, we sought to accomplish the first electropolymerization of a monomer-monolayer as a precursor to an electrically conducting poly(2-pentadecylaniline).

Prior to formation of the interface monolayer the cleanliness of the interface was confirmed by stability of the interfacial pressure after suction purification. Several control experiments were carried out to ensure that the observed changes in interfacial pressure were related to the formation of polymer during electrolysis and not to a reaction forming surfactants from the organic solvent. Figure 2 shows the temporal stability of the interfacial pressure of a cyclohexane-sulfuric acid interface without any 2-pentadecylaniline when a potential of 2 V was applied with stainless steel electrodes immersed into the interface. No change of the interfacial pressure can be observed. A second stability test probed the interfacial pressure for monomer that is trapped at the interface under no applied voltage. No change in interfacial pressure with time was observed with monomer spread and no potential applied. A third stability test involved immersing the anode into the upper cyclohexane layer and the cathode into the interface. After introducing the monomer to the interface a potential of 2 V was applied. No change of interfacial pressure with time could be observed over 60 min.

Figure 2

The change in interfacial pressure during electrochemically induced polymerization of a monolayer of 2-pentadecylaniline at the 4 M sulfuric acid-cyclohexane interface is shown in Figure 3. At $t = 2$ min monomer solution was injected into the interface. Upon contact the monomer is protonated and a salt is formed that spreads quickly, rapidly increasing the interfacial pressure to ca. 42 mN/m. The monomer salt is much less soluble in cyclohexane. The system was then allowed to stand for 23 minutes for equilibration as the pressure relaxed to 40 mN/m and no further change in interfacial pressure could be observed.

The interfacial pressure decrease directly after spreading can be attributed to the fact that the monomer is protonated and the compound diffuses laterally to become equally distributed across the interface. Before equilibrium is reached deprotonated monomer diffuses into the organic phase, decreasing the number of molecules present at the interface, and thus decreasing the interfacial pressure. Previous work at the air-water interface has shown that the monomer is much less soluble in the aqueous phase.⁴

Application of 1.8 V across the two electrodes immersed at the interface led to a current of 120 mA. An immediate increase in interfacial pressure is observed due to changes at the interface. A polymer is formed that has a higher surface mass density (i.e., smaller mean molecular area per repeat unit) compared to its monomer, which has also been observed for the polymerization of the same compound at the air-water interface.⁴ The mean molecular area per molecule decreases thus leading to empty sites at the interface, and additional monomer from the solution diffuses to the interface and

increases the interfacial pressure. The oligomer and polymer formed during the reaction are less soluble in cyclohexane and remain at the interface.

With all sulfuric acid subphase concentrations investigated (0.1 M, 0.4 M, 1.0 M, 4.0 M) the interfacial pressure is seen to increase monotonically with time when the stainless steel electrodes were immersed at the interface, and a potential of at least 1.5 V was applied across the interface. The reaction was complete and a new equilibrium was reached after about 2 h. The effect of increasing the acid concentration was to increase the interfacial tension, and therefore, the amount of monomer trapped before reaction. The measured interfacial pressure change upon polymerization was largest for the 0.1 M sulfuric acid subphase concentration. The acid subphase concentration did not substantially effect the time until the new equilibrium was reached.

To ensure that the reaction is confined to the interface the electrodes were lifted to form a meniscus with the subphase, as shown in Figure 1B. If one electrode was in the organic phase only, a very low current (less than 0.6 mA), no change in interfacial pressure, and no formation of ions in any phase could be observed. The collected product only showed a monomer peak in the GPC. The results indicate that no polymerization takes place in the organic phase. Control experiments, using the same system and immersing both electrodes into the subphase after the above mentioned results were obtained, proved that polymerization was possible, i.e., a change in interfacial pressure could be observed and polymer could be collected. Previously published experiments⁴ showed, that the

monomer is essentially insoluble in the aqueous electrolyte subphase. Additionally, the electrodes generally only touched the plane of the interface and were not immersed in the subphase. These results indicate that the polymerization is confined to the interface.

Experiments were carried out to get a better understanding of the reaction process. It was found that there is polymer formed only when a stainless steel electrode is used as anode. No change in interfacial pressure could be observed and no polymer could be formed with pure metal electrodes (platinum, iron, zinc, cobalt, vanadium, nickel, chromium and silver). While applying a voltage it could be observed that the investigated pure element anode materials produce mostly oxygen. The amount of oxygen produced at the stainless steel anode, however, was significantly less and the subphase solution turned yellow due to ferric ions that were produced. Due to an overpotential for oxygen formation at the stainless steel electrode, ions of the metals in the stainless steel are formed. Ferric ions are most prevalent and have an appropriate oxidation potential to oxidize and polymerize the monomer. With the pure iron anode no ferric ions were formed, only the formation of oxygen could be observed.

To confirm that the reaction is induced by electrogenerated Fe^{3+} , the stainless steel anode and platinum cathode were immersed at an interface without any monomer spread. A potential of 3 V was applied resulting in a current of 26.8 mA with a 0.1 M sulfuric acid subphase concentration. The subphase changed its color from clear to yellow due to the ferric ions formed but no change of interfacial pressure could be observed, as was expected from the stability tests. After 20 min the electrodes were taken out, the monomer was

introduced and the interfacial pressure was monitored. Polymer was formed.

The above results prove that the reaction is likely to be electrochemically mediated in that the application of a voltage across the interface releases metal ions from the electrode that chemically polymerize the monomer. Further evidence is that the monomer is successfully polymerized at this interface by FeCl_3 .⁹

Reaction Control on Interfacially Grown Polymer

Figure 4 shows that reaction control is possible at dilute acid subphase concentrations by switching the potential on and off. The interfacial pressure varied with the subphase acid strength. After introduction of the monomer to the interface with 0.1 M sulfuric acid, a lower value of interfacial pressure (2 mN/m) is obtained than with 4.0 M sulfuric acid in the subphase. This is due to the lower ionic strength of the subphase that reduces the amount of monomer that is trapped at the interface, thus decreasing the value of the interfacial pressure.

After equilibration, a voltage is applied starting at 25 min. In 0.1 M sulfuric acid the current with an applied voltage of 1.8 V is about 1 mA. Since the current is low, it is possible to start and stop the reaction by switching the voltage on and off. In this figure, the voltage was turned off at 45 min and turned on again at 85 min. There is a delay in starting and stopping the reaction after switching the voltage on and off as the concentration of the oxidizing ions has to reach a concentration that results in a potential that is higher than

the oxidation potential of 2-pentadecylaniline. As the reaction continues the concentration of ferric ions decreases and ferrous ions increases, thus, lowering steadily the oxidation potential of the subphase until the reaction stops.

The decrease in the interfacial pressure after turning off the voltage at 45 min, is assumed to be connected with the diffusion of oligomers from the interface into the organic phase, until an equilibrium between oligomer and monomer is reached. This is also specific for the 0.1 M sulfuric acid subphase. At 4.0 M a decrease never could be observed. We assume this to be due to the protonation of the compound and the increase in interfacial tension at higher acid concentrations.

Figure 4

Polymer Characterization

The polymer produced was analyzed by GPC. For all polymer formed the weight average M_w was 3500 using a calibration of polystyrene. It should be noted that a small amount of residual monomer was always observed.

A cyclic voltammogram as a function of scan rate of the interfacially synthesized poly(2-pentadecylaniline), solution cast onto an ITO electrode, is shown in Figure 5. Independent of the electrolyte employed (CH_3CN or aqueous acid), only a single reversible redox process is observed with an $E_{1/2}$ of + 0.15 V vs. Ag/Ag^+ . Accompanying this redox process is a color change from green at low

potential to blue at high potential. This is in contrast to polyaniline and poly(2-methylaniline), which exhibit two redox processes when examined in 0.1 M HCl, 2.4 M HCl and 1.0 M H₂SO₄.^{15,16} Under these conditions, poly(2-methylaniline) switches from yellow to green to blue-violet as the potential is swept from fully reduced to fully oxidized. Poly(2-ethylaniline), on the other hand, exhibits only one redox process when examined¹⁶ in 1 M H₂SO₄ ($E_{1/2} = +0.36$ V vs. SCE) and two poorly resolved redox processes centered around +0.4 V vs. SCE when examined¹⁵ in 2.4 M HCl.

Figure 5

Optoelectrochemical spectra of poly(2-pentadecylaniline) were sequentially obtained to more fully probe the available oxidation states. An optoelectrochemical spectrum of solution cast interfacially prepared, poly(2-pentadecylaniline) examined in TBAP/CH₃CN is shown in Figure 6. Similar results are observed in acidic media. The as cast polymer shows two transitions at 1.7 eV and 4.0 eV. As the potential is stepped from highly reducing (-0.7 V) to highly oxidizing (+1.4 V), there is an increase in the absorption at 1.7 eV and decrease in the absorption at 4.0 eV. At the same time, a new absorption at 3.25 eV begins to appear. It should be noted that these spectral changes are small relative to those seen for polyaniline, poly(2-methylaniline), and poly(2-ethylaniline).^{15,16} Interestingly, an isosbestic point is observed in the optoelectrochemical results for poly(2-pentadecylaniline) and, in agreement with the cyclic voltammetrically observed green to blue color change, suggests that

only two redox states are electrochemically accessed. Treatment of the CHCl_3 solution of poly(2-pentadecylaniline) with a strong chemical reductant (e.g. hydrazine) converts the polymer to a yellow state, but this chemical reduction is not effective on cast films. Polymer films prepared by direct electropolymerization of pentadecylaniline in CH_3CN electrolyte behave similarly.

Figure 6

In general, there are three commonly accessible redox states in polyaniline which are defined as leucoemeraldine (fully reduced), emeraldine (half-oxidized) and pernigraniline (fully oxidized).

Figure 7

Correlation of the results presented for poly(2-pentadecylaniline) indicates that the leucoemeraldine form is not attained in the electrochemical experiments. The cyclic voltammetric switching occurs between the emeraldine and the pernigraniline forms of the polymer. It is expected that the long alkyl chain will have a strong impact on the chemical environment within the film which makes access to the fully reduced (and least polar) form of the polymer difficult. This extreme case is not surprising when compared to the results observed for the methyl and ethyl substituted polyanilines. While all three redox states are observable in these polymers, there is considerably less change during redox switching of poly(2-ethylaniline) relative to poly(2-methylaniline).¹⁶

Conclusions

Electrochemically mediated polymerization of 2-pentadecylaniline with its bulky alkyl sidechain could be observed at the aqueous sulfuric acid - cyclohexane interface as well as electrochemically in an acetonitrile solution. The interfacially grown polymer had a molecular weight of 3500 compared to polystyrene standard. Both polymers formed were electroactive.

The reaction for the interfacially grown polymer could be controlled at low sulfuric acid subphase concentrations and a small voltage by turning the voltage applied across the interface on and off.

The polymer could be fully reduced to leucoemeraldine chemically in solution. Electrochemical reduction of a thin film of poly(2-pentadecyl aniline) allowed only one step for reduction: pernigraniline was reduced to emeraldine. The yellow leucoemeraldine state could not be formed in a thin film.

Acknowledgments

The authors would like to acknowledge the Deutsche Forschungs Gemeinschaft and the Office of Naval Research for financial support of this work.

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Figure Captions

Fig. 1 Experimental setup for interfacial polymerization of 2-pentadecylaniline, whole system (A) and magnification of the meniscus formed by the aqueous phase at the inserted metal electrode, and at the needle of the syringe (B).

Fig. 2 Interfacial pressure baselines for experiments with 0.1 M sulfuric acid as subphase. Curve A: Measurement of the interfacial pressure vs. time with electrodes in the organic phase only, with compound spread and voltage applied. Curve B: Measurement of the interfacial pressure with electrodes inserted at the interface and voltage applied, but no monomer spread.

Fig. 3 Interfacial pressure change during polymerization of a monolayer of 2-pentadecylaniline at a 4.0 M sulfuric acid-cyclohexane interface using a stainless steel anode and a platinum cathode. Initial theoretical mean molecular area (Interfacial area divided by number of molecules spread, assuming all spread molecules are trapped at the interface) $MMA = 25 \text{ \AA}^2$.

- 1) Spreading of the compound without applied voltage. (left scale).
- 2) Reaction with turning on the voltage at 25 min (right scale).

Fig. 4 Reaction control at dilute acid interfaces. Plot of interfacial pressure vs. time. The voltage was turned on at 25 min. (marker 1) and turned off at 45 min. (marker 2) and turned on again at 85 min (marker 3).

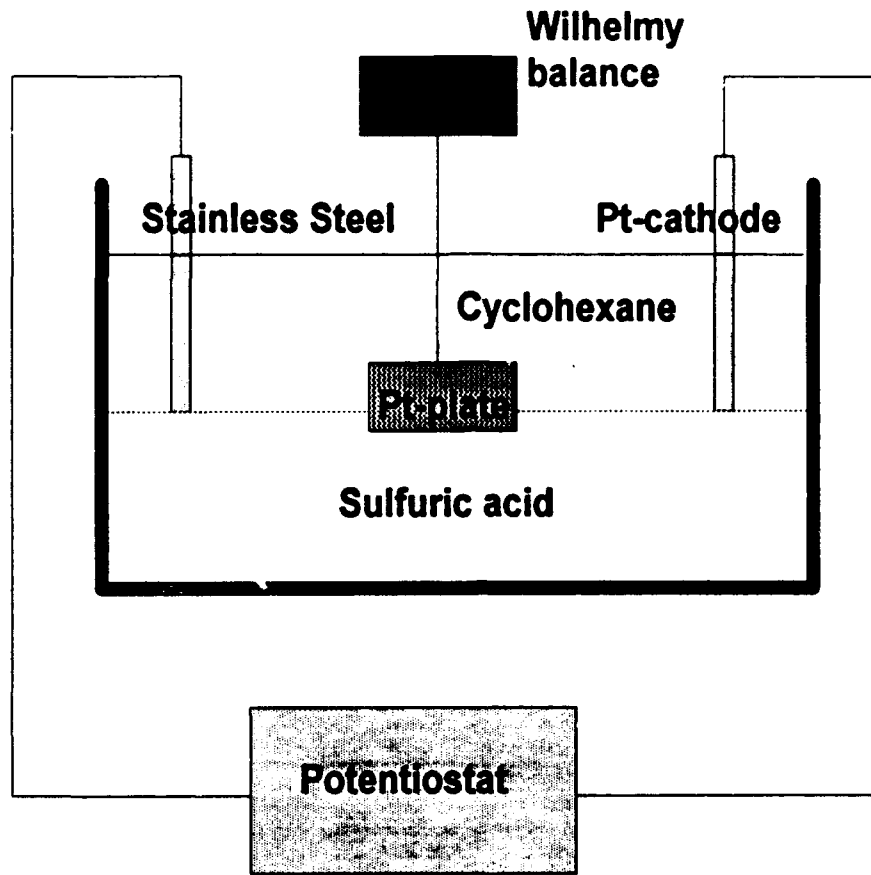
Fig. 5 Cyclic voltammograms of interfacially synthesized poly(2-pentadecylaniline) run in TBAClO₄/CH₃CN. Polymer film produced by solution casting with chloroform on platinum. Scan speed A= 25 mV/s, B=50 mV/s, C=75 mV/s, and D=100 mV/s.

Fig. 6 Optoelectrochemical spectra for interfacially synthesized poly(2-pentadecylaniline). Polymer film produced by solution casting with chloroform on ITO. Applied potentials vs. Ag wire: a) -0.7 V, b) 0.3 V, c) 0.7 V, d) 0.9 V, e) 1.2 V, f) 1.4 V. Arrows indicate change of signal intensity with increasing oxidation potential.

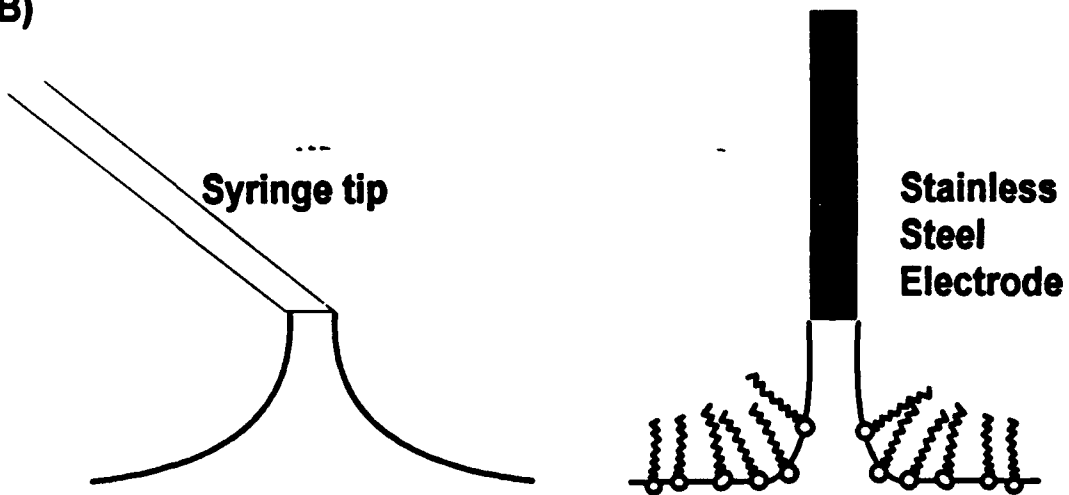
Fig. 7 Chemical structures that can theoretically be drawn for poly (2-pentadecylaniline) in different oxidation states. A) leucoemeraldine-like form, B) emeraldine-like form, and C) pernigraniline-like form.

I

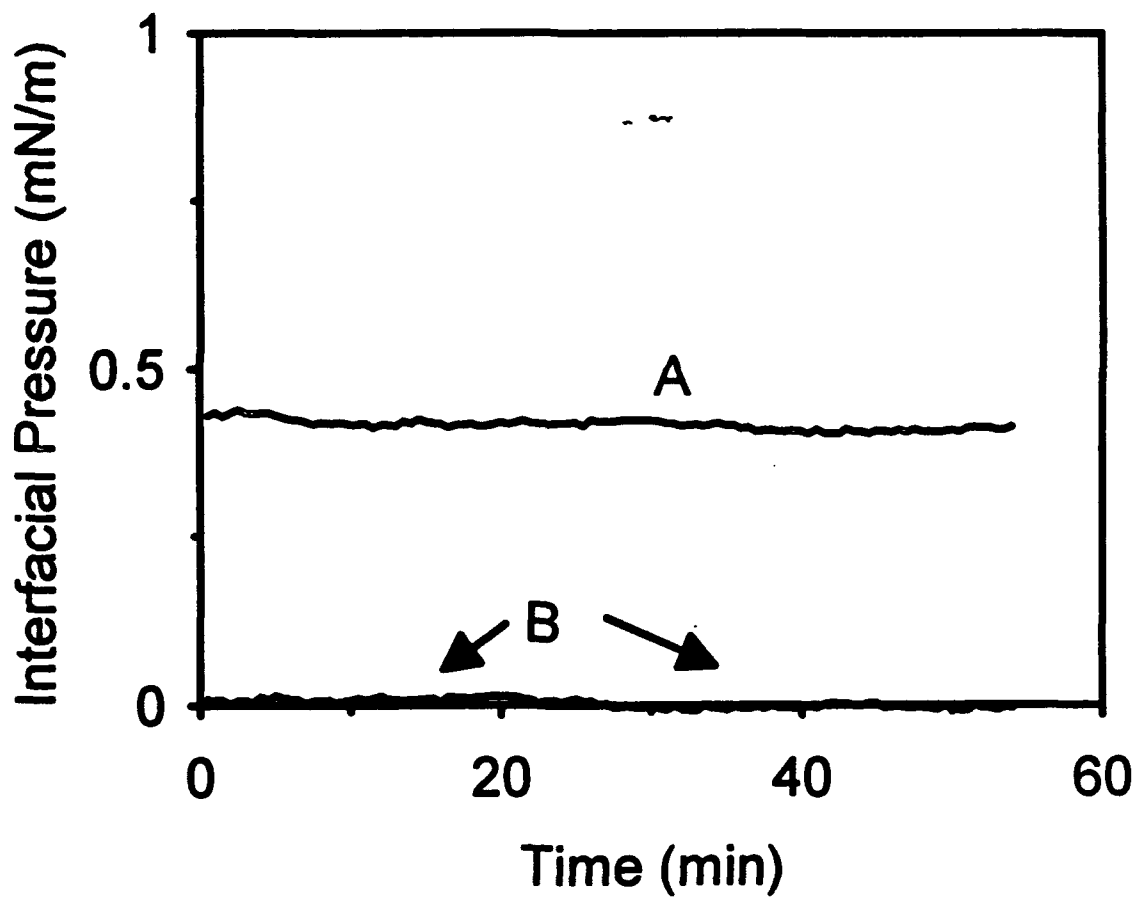
(A)

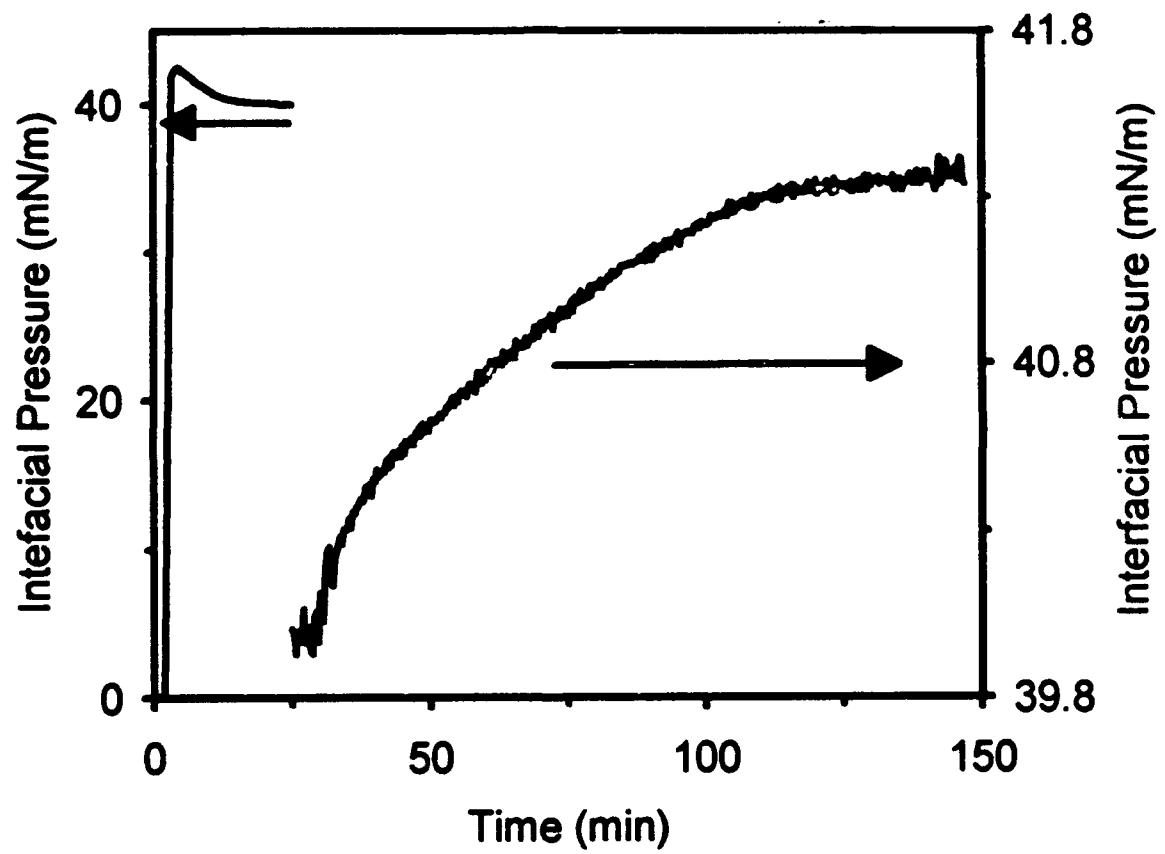


(B)

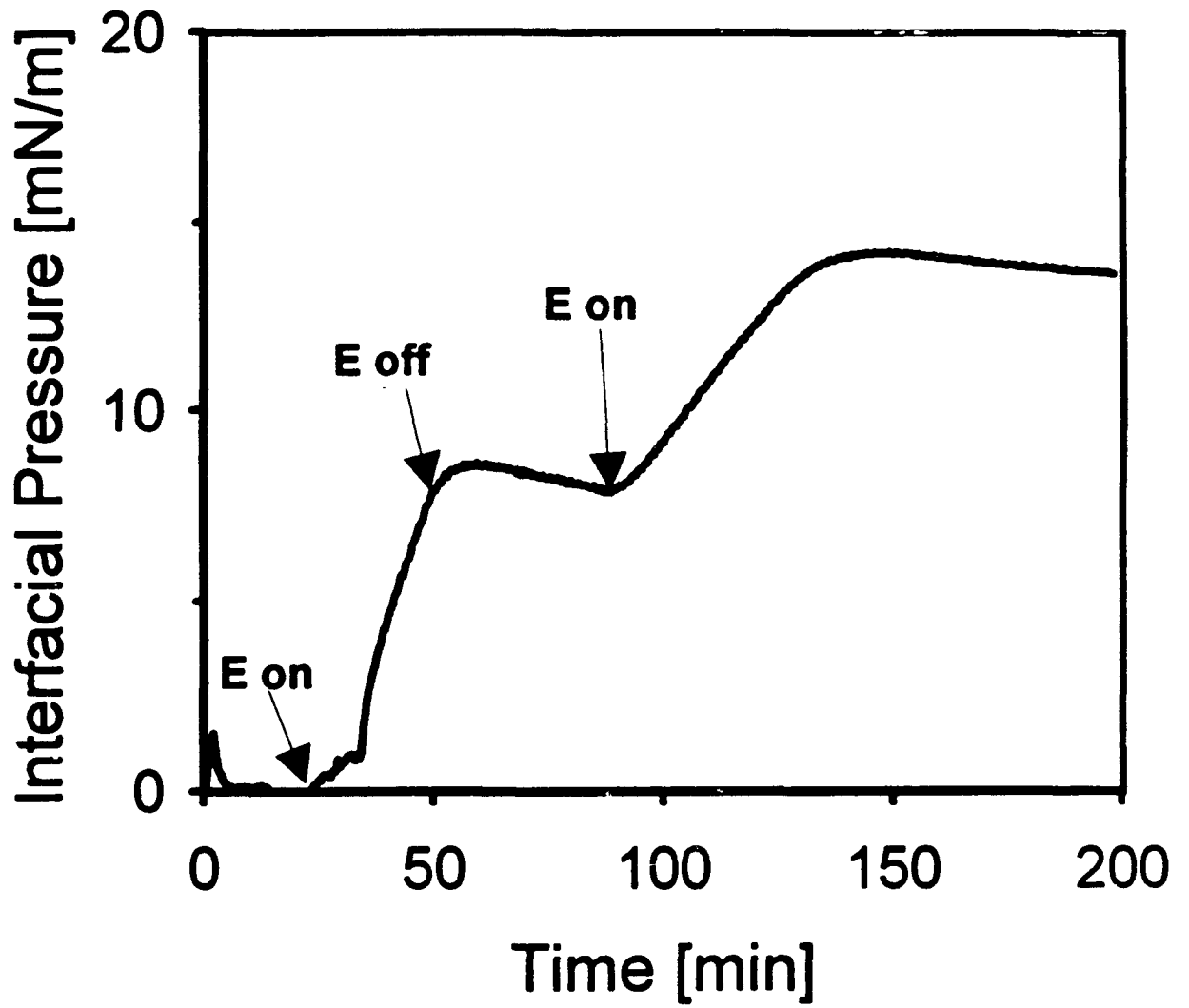


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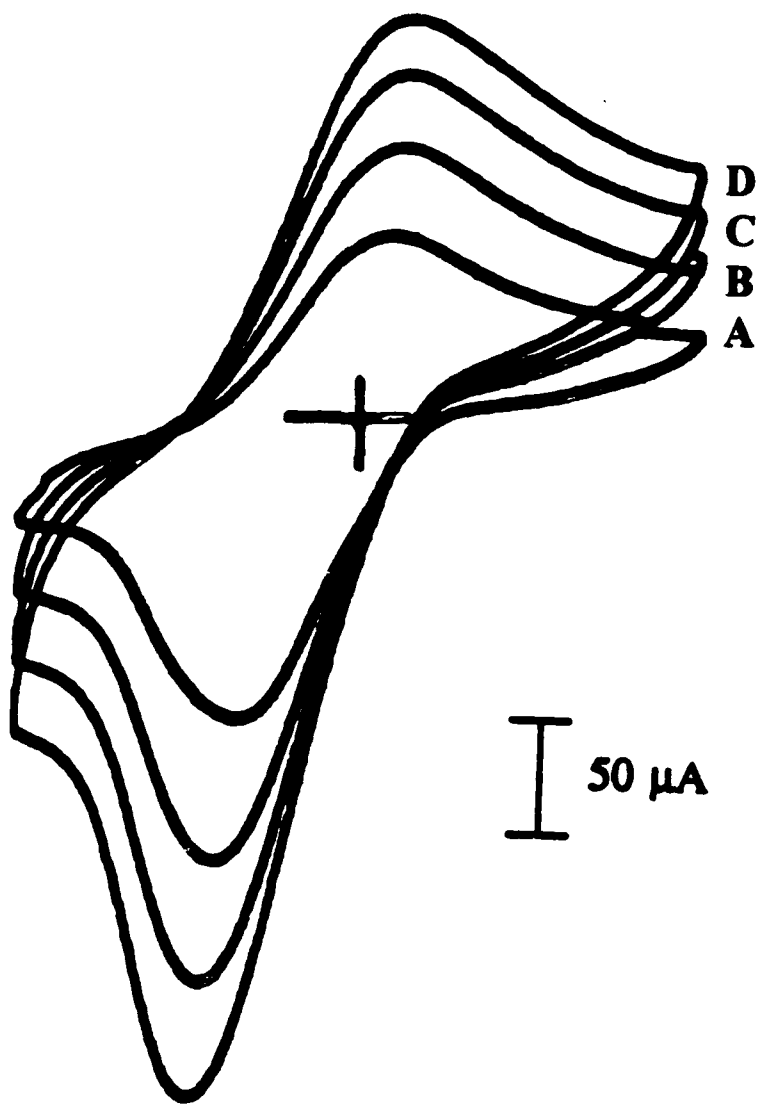
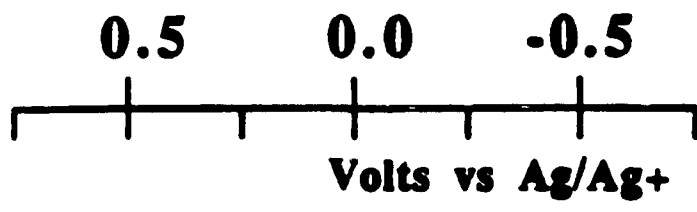




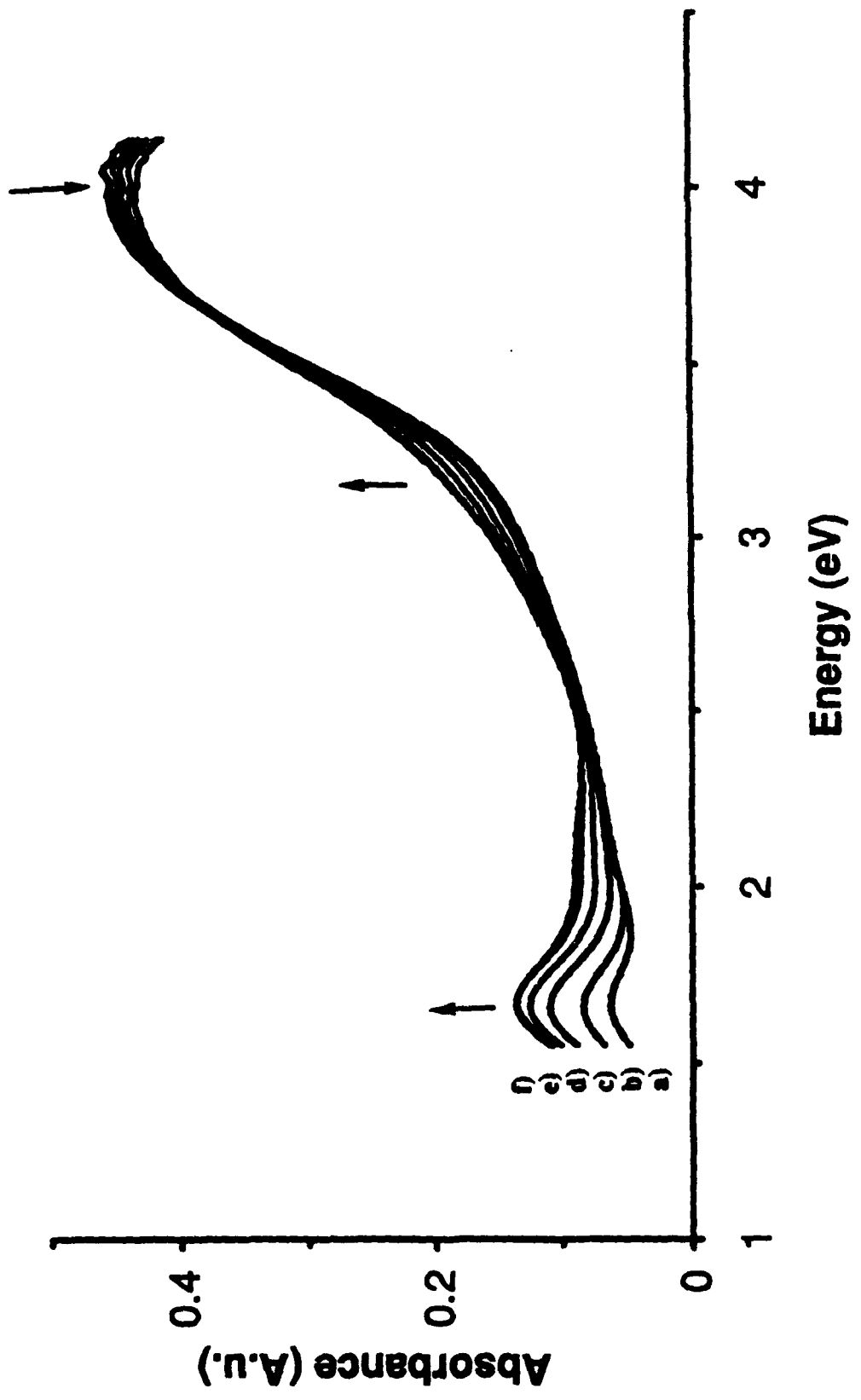
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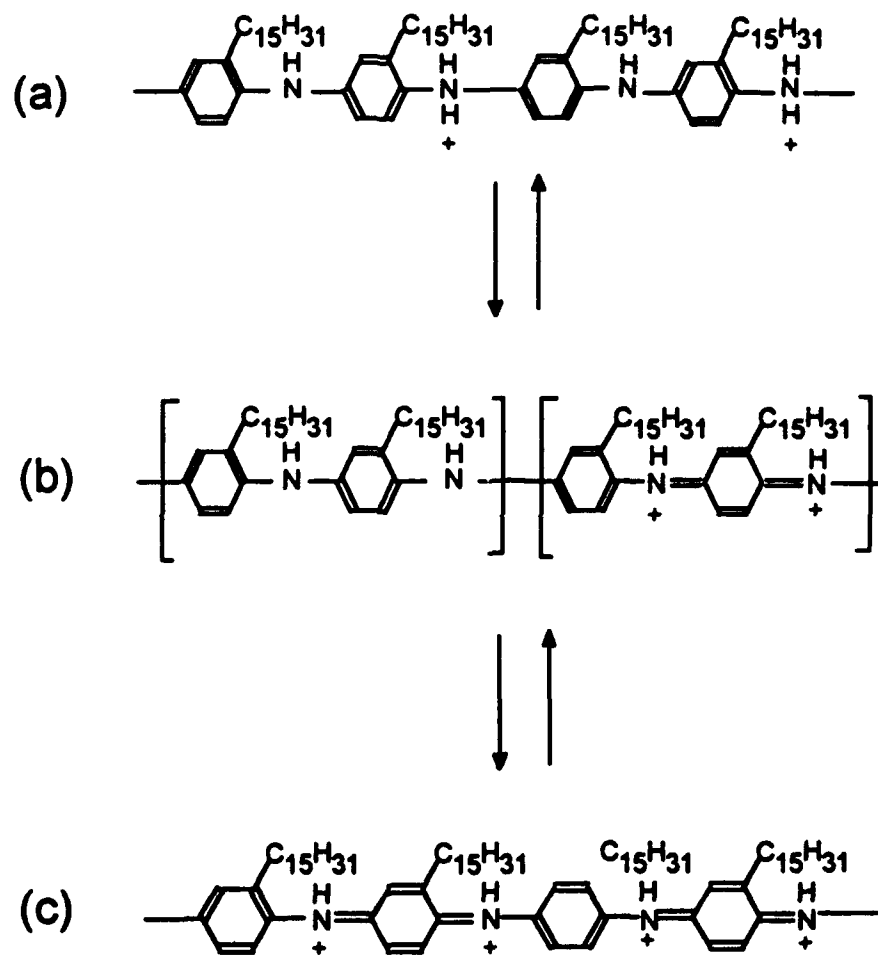


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VI





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