②

OFFICE OF NAVAL RESEARCH
Grant No. N00014-91-J-1655
R&T Code 4132058---02

TECHNICAL REPORT NO. 24

Chemical Polymerization and Langmuir-Blodgett Techniques, 2: The Polymerization of Monolayers of 3-Substituted Pyrroles

by

W.M. Sigmund, C. Marestin, S. Keil, H. Zhou and R.S. Duran

Center for Macromolecular Science and Engineering
Department of Chemistry
University of Florida
Gainesville, FL

M.Z. Elsabee

Department of Chemistry
Cairo University
Egypt

and

J. Rühe and G. Wegner

Max-Planck Institute for Polymer Research
Mainz, Germany

34pp

93

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE 12/9/93

3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE

Chemical Polymerization and Langmuir-Blodgett Techniques 2: the Polymerization of Monolayers of 3-Substituted Pyrroles

5. FUNDING NUMBERS

Grant No. N00014-91-J-1655

6. AUTHOR(S)

W.M. Sigmund, C. Marestin, S. Keil, H. Zhou, R.S.Duran, M.Z. Elsabee, J. Ruhe and G. Wegner

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

R. S. Duran
Department of Chemistry
University of Florida
Gainesville, Florida 32611

8. PERFORMING ORGANIZATION REPORT NUMBER

24

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Dr. Kenneth J. Wynne
Code 1113PO, Office of the Chief of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000
(703) 696-4409

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

submitted to Macromolecules

12a. DISTRIBUTION/AVAILABILITY STATEMENT

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Derivatives of 3-substituted pyrroles were spread at the air-water interface. Stable films could be obtained for pyrroles with side chains containing more than 10 carbons. 3-Hexdecanoyl pyrrole could not be polymerized as a monolayer whereas the alkyl derivatives could be polymerized successfully without having additional monomer in the subphase. It was possible to yield a true two-dimensional polymer monolayer film, without chain overlapping. The monolayers could be transferred onto hydrophobized substrates with transfer ratios being about unity. The polymers formed were soluble in chloroform and THF. Molecular weight averages were obtained by GPC ranged from 3,500 to 6,000 when polymerized on ammonium peroxodisulfate and 5,000 to 15,000 when polymerized on ferric chloride subphase solutions. 1H-NMR indicates that the polymerization is highly regular, leading to a constitutionally ordered 2,5 poly(3-alkyl pyrrole).

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

[redacted]submitted to Macromolecules Sigmund, Duran, 11/03/93

Chemical Polymerization and Langmuir-Blodgett Techniques, 2

The Polymerization of Monolayers of 3-Substituted Pyrroles

W. M. Sigmund a), C. Marestin a), S. Keil a), H. Zhou a), M. Z. Elsabee b), J. Rühe, G. Wegner c) and, R. S. Duran *a)

a) Dept. of Chemistry, University of Florida, Gainesville, FL 32611-2046, USA

b) Dept. of Chemistry, Cairo University, Egypt

c) Max-Planck-Institute for Polymer Research, Mainz, Germany

Abstract

DTIC QUALITY INSPECTED 5

Derivatives of 3-substituted pyrroles were spread at the air-water interface. Stable films could be obtained for pyrroles with side chains containing more than 10 carbons. 3-Hexadecanoyl pyrrole could not be polymerized as a monolayer whereas the alkyl derivatives could be polymerized successfully without having additional monomer in the subphase. It was possible to yield a true two-dimensional polymer monolayer film, without chain overlapping. The monolayers could be transferred onto hydrophobized substrates with transfer ratios being about unity. The polymers formed were soluble in chloroform and THF. Molecular weight averages obtained by GPC ranged from 3,500 to 6,000 when polymerized on ammonium peroxodisulfate and 5,000 to 15,000 when polymerized on ferric chloride subphase solutions. ^{1}H-NMR indicates that the polymerization is highly regular, leading to a constitutionally ordered 2,5 poly(3-alkyl pyrrole).

Introduction

Due to their air stability and high electrical conductivity, polyaniline and polypyrrole have been the focus of great attention.[1,2] Through functionalization with appropriate side groups, these otherwise poorly soluble polymers can be made soluble in common organic solvents in the neutral state or when the degree of oxidation is low.[3] Furthermore, highly oriented thin films of these functionalized polymers can be made by the Langmuir-Blodgett (LB) technique.[4] These LB films show interesting anisotropic optical and electrical properties. Indeed, such films may prove to be useful in understanding low dimensional conductors. Some groups have successfully spread these types of conducting polymers at an air-water interface and built up multiple layers by LB methods.[5,6] However, the resulting films can always have substantial numbers of defects caused by overlapping chains and thus a less well defined two-dimensional (2-D) nature.

A method of forming a true 2-D film is to polymerize a preformed highly oriented monolayer of monomer. Under these conditions an ideal non-intersecting 2-D random walk conformation can be formed. Monolayers of some 2-alkyl anilines on a Langmuir-trough have been polymerized in our lab.[7,8] On the other hand, 3-alkyl pyrroles have been reported to be polymerizable on the LB trough only when a large amount of pyrrole was dissolved in the aqueous subphase.[5,6] The resulting thin films had very interesting properties but were not monolayers in the conventional sense.

In the present study, three 3-substituted pyrrole monomers with different side chain lengths and moieties were investigated regarding their spreading and polymerization behavior on the LB-trough. The purpose was to find a compound that can be regularly ordered polymerized as a monolayer. Additionally, its polymerization product should be transferable via LB or Langmuir-Schäfer technique onto solid substrates. The chemical structures of the investigated compounds are shown in Figure 1.

<Insert Figure 1 about here>

Experimental Part

The synthesis of the monomers, 3-decyl pyrrole and 3-hexadecyl pyrrole, was based on previously published procedures.[3] ^{1}H-NMR and ^{13}C-NMR 200-MHz spectra were obtained with a Varian XL-Series NMR spectrometer system at 75 °C in deuterated tetrachloro ethane.

<Insert Figure 2 about here>

The NMR-spectra of 3-hexadecyl pyrrole and its carbonyl derivative, 3-hexadecanoyl pyrrole are shown in Figure 2. The compounds are distinguishable due to the deshielding effect of the carbonyl group on the proton attached to position 2 of the pyrrole ring in 3-hexadecanoyl pyrrole (7.4 ppm compared to 6.55 ppm after the reduction). The ^{13}C spectra also show a deshielding effect on carbons 2 and 5 (117.5 and 114.5 ppm shift to 124 and 120 ppm) as well as on the methylene groups.)

The melting points of 3-hexadecyl and 3-hexadecanoyl pyrrole were 42° and 77°C, respectively. The compounds were purified by fractional distillation and flash chromatography to eliminate impurities. All compounds were found to be pure by TLC and FTIR. Traces of the carbonyl compound in the 3-hexadecyl pyrrole could be identified by a very weak band at about 1730 wavenumbers. Elemental analysis of the 3-hexadecyl pyrrole was as follows: calc.

C=82.98, H=12.19, N=4.84%; found C=82.62, H=12.74, N=4.76%, respectively.

Monolayers and polymerization were studied using a commercially available computer controlled film balance (KSV 5000, KSV Instruments, Finland) equipped with floating barrier and Wilhelmy balance pressure measurement system, temperature controller, and pH measurement head. Monolayers were obtained by spreading solutions of the monomers dissolved in chloroform (ACS Spectro Grade, Eastman) at concentrations of approximately 0.5 mg/ml. The balance was zeroed before addition.

Isotherms of surface pressure versus mean molecular area per repeat unit (Mma) were measured at 23°C on Milli-Q® water with a specific resistance of greater than 18 MΩ/cm for the monomers. For polymerization and studies of the polymer, subphase solutions were made with A.C.S. reagent grade chemicals and Milli-Q® water. Subphase oxidizing agents were ferric chloride (0.005 - 0.3 M), ammonium peroxodisulfate (0.03 M) or a mixture of sulfuric acid (0.1 M) and ammonium peroxodisulfate (0.03 M). After polymerization, materials collected from the trough surface for further analysis were washed with water, alcohol and again with water, then dissolved in chloroform and after evaporation dried and stored in a desiccator under nitrogen.

The transfer of the monolayers from the Langmuir-trough onto solid substrates was studied with 3-hexadecyl pyrrole and its polymerization product. Different subphase solutions (oxidizing, non oxidizing, acidic, neutral and basic), substrate surfaces (quartz, glass, silicon wafer - hydrophilic and hydrophobized), dipping speeds (1 - 50 mm/min), dipping surface pressures (0.2 - 40 mN/m) and polymerizing conditions (surface pressure, subphase solutions) were examined.

UV-vis spectra were recorded in chloroform solution with a Perkin Elmer Lambda-9 spectrophotometer. IR spectra were recorded using a FTS-40A FTIR-spectrometer (Bio-Rad Lab. MA). Gel permeation chromatography (GPC) data 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 x 300 mm 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

Monomer

All monomers could be spread at the air-water interface using a chloroform solution. Typical compression isotherms on a water subphase are shown in Figure 3.

<Insert Figure 3 about here>

The onset of the isotherm of 3-decyl pyrrole is at a mean molecular area per molecule (Mma) of about 36 Å^2. The monolayer collapses at a Mma of about 21 Å^2 and an applied surface pressure of about 22 mN/m. The shape of the isotherm is analogous to that observed in similar substituted anilines.[7] Hysteresis and isobaric stability measurements, however, proved that films of the 3-decyl substituted monomer were unstable when a surface pressure was applied. The aliphatic tail of this monomer renders it too hydrophilic to form a stable monolayer under compression.

3-Hexadecyl pyrrole formed stable monolayers with a surface pressure onset point of 25.6 Å^2. The monolayer collapse happens at about 20 Å^2 with a surface pressure of about 50 mN/m. These values are comparable to those of stearic acid.[9] Therefore, it may be supposed that the long alkyl chain of this monomer is well-packed in the condensed region of the isotherm and almost no contribution of the pyrrole ring has to be considered.

Figure 3 also shows the isotherm of 3-hexadecanoyl pyrrole. It compares well with literature values for similar compounds, though shifted to slightly higher areas.[10] In comparison tc the non-carbonyl compound it is shifted to higher surface areas and has a lower collapse pressure.

Polymerization

Isobaric polymerization was done using subphase solutions of ferric chloride and acidic and nonacidic ammonium peroxodisulfate. The alkyl-substituted monomers could be polymerized, whereas no polymer could be collected for 3-hexadecanoyl pyrrole. The last one may not polymerize, probably due to the electron withdrawing nature of the carbonyl group.

The reaction that takes place at the interface can be monitored directly. The surface area is observed as a function of the reaction time at constant surface pressure. This is similar to a procedure used for functionalized anilines in previous publications.[7]

<Insert Figure 4 and 5 about here>

Figure 4 shows results from a polymerization of 3-hexadecyl pyrrole on a 0.05 M $FeCl_3$ subphase at 23°C where the surface pressure was kept constant at 15 mN/m. Figure 5 displays the data for the polymerization of 3-hexadecyl pyrrole on a 0.03 M ammonium peroxodisulfate subphase at 23°C where the surface pressure was kept constant at 10 mN/m. In both cases, the polymerization was complete in about 20 minutes. During the reaction, both the surface area and the barrier speed were observed to decrease as the time of reaction increased.

The area contraction during the polymerization reaction is analogous to the volume contraction seen by dilatometry in typical polymerization reactions. After polymerization, the resulting monolayer films for both alkyl substituted compounds were stable, i.e., negligible change in molecular area with time at various applied surface pressures. It should be noted that no polymerization was observed when the pyrrole was spread on pure water and compressed.

The area change observed during polymerization is due, in part to the replacement of a Van der Waals distance between adjacent monomers with a chemical bond due to polymerization. The area change, however, must also be indicative of a conformational change of the monomer upon polymerization.

During polymerization on a ferric chloride subphase a decrease of about 13Å^2 per molecule in surface area is observed. For ammonium persulfate, with or without sulfuric acid, the decrease is about 4 Å^2 per molecule. So far, it is not clear what this difference in surface area change for the two subphase solutions can be attributed to. A value of 17 Å^2 per repeat unit for the polymerization product on ferric chloride requires a different packing structure for the alkyl chains than just a dense ordered packing of orientationally aligned rods. Previous results on polypyrroles have indicated a helical backbone conformation is produced by polymerization in solution.[12] Nonetheless, the mean molecular area change can be used to monitor the reaction of these substituted pyrroles in real time.

In general, the pyrroles seemed more reactive on the LB trough than 2-substituted anilines. Unlike polyaniline, however, which shows an auto acceleration effect upon polymerization[13,14] in this case, surface area and barrier speed decreased continuously as the polymerization progressed. Initial GPC measurements of molecular weight vs. conversion are in agreement with a non-classical chain growth mechanism.

Polymer

After polymerization the monolayer can be characterized by hysteresis experiments, i.e., the monolayer is repeatedly expanded and compressed. For 3-decyl pyrrole the monolayer film could be expanded and recompressed with little hysteresis after polymerization. This is different from a polymerized monolayer of 3-hexadecyl pyrrole, as shown in Figure 6 on a subphase containing 0.1 M sulfuric acid and 0.03 M ammonium peroxodisulfate.

<Insert Figure 6 about here>

On expanding the monolayer an increase in surface area of about 3Å^2 per molecule is observed for the polymerization product on the ammonium persulfate subphase. The same is true for the point of onset of the first recompression of the polymerized monolayer. This seems to be contradictory since during polymerization the Mma of the monomer monolayer decreased. This apparent contradiction may be explained by the following. First, the isotherm of the monomer is dependent on the salt concentration and the type of salt in the subphase. By adding, for example, ferric chloride in concentrations higher than 0.05 M an increase in Mma is observed.[6] This observed increase in surface area may be interpreted as a phase transition from a liquid condensed to a liquid expanded layer depending on the ionic *strength of the subphase solution.*[11]

Second, after polymerization, the monolayer may rearrange and demix on expansion, simultaneously allowing the pyrrole ring to "lie almost flat" on the surface as the all-transoidal polymer structure would require.

<Insert Figure 7 about here>

The resulting pyrrole polymers were characterized by several techniques. As the material is not highly oxidized it was possible to obtain NMR spectra of the polymer. The ^{1}H-NMR spectra of the obtained polymer is in good agreement with the proposed structure as depicted in Figure 7. It shows one peak at 7.26 ppm, which can be attributed to the proton in the 4 position of the pyrrole moiety. This indicates that the polymer formed is very highly 2,5 linked. The NMR also clearly shows signals due to the alkyl chain of the substituent. How strongly the resonance frequency of the aromatic proton is shifted depends on the degree of oxidation of the polymer backbone. It should be noted that no signals due to an end group are visible.

<Insert Figure 8 about here>

The IR spectrum is in good agreement with that of poly(3-alkyl pyrroles) synthesized by electrochemical or conventional synthesis with ferric chloride in solution.[15] However, it should be noted that highly oxidized material, such as polymer obtained by electrochemical means, shows a strong IR absorption at 4000 to 1600 cm^{-1}. The broad featureless band has been attributed to a free charge carrier absorption. In highly oxidized material, in fact, the intensity of this band is so strong that it completely covers the bands due to the C-H vibrations of the alkyl side chain. In the material synthesized as described here, the bands due to vibrations in the side chains are still visible. A band at 1730 wavenumbers indicates that some of the pyrrole moieties were oxidized, too. We expect this to be only a minor amount since the NMR does not indicate any additional compounds than the regular structure and the carbonyl moiety is known to have a very high extinction coefficient.

<Insert Figure 9 about here>

Figure 9 shows the UV-vis spectra of 3-hexadecyl pyrrole (curve a) and its product (curve b) after the polymerization on the LB-trough. Both alkyl-substituted monomers had similar UV-vis spectra, one absorption band at 235 nm. From these data it appears that the alkyl side chain length does not effect the UV-vis spectra of monomers and polymers of alkyl substituted pyrroles. However, the UV-vis spectra of the polymers were completely different from those of the monomers and showed a broad absorbance in the range of 200 nm to 800 nm with a peak at 400 nm and a plateau at and beyond 680 nm. An additional peak at 235 nm might be attributed to unreacted monomer that is left in the product. Whereas the optical spectrum of the obtained material clearly indicate that polymer is formed, they also show that the material is not highly oxidized. The spectra are in good agreement with those of poly(3-alkyl pyrroles) at intermediate degrees of oxidation.[15] Indeed the color of the polymer in chloroform was dark greenish, unlike the dark black color of solid polypyrrole.[16] It should be noted that if the polymer formed was left on the trough under air for several hours further oxidative degradation of the poly(3-alkyl pyrroles) occurred which decreased the polymer yield and caused the color of the products to turn brown and smaller molecular weights were measured. This also agrees with the behavior of polypyrroles synthesized by conventional means, where also only highly oxidized material is stable under ambient conditions. With decreasing degree of oxidation the stability strongly decreases and neutral polypyrrole derivatives degrade in air almost instantaneously.

The polymerization products under the conditions shown in Figures 4 and 5 were also analyzed by GPC. The UV-detector recorded two peaks for the polymerization products: one corresponding to monomer and the other corresponding to polymer with a polystyrene-equivalent molecular weight average (M_W) of approximately 5,000 to 15,000 for polymerization on ferric chloride and 3,500 to 6,000 for polymerization on ammonium peroxodisulfate subphase solution. No third peak could be found that would correspond to the alkyl substituted 2,5-bis(2-pyrrolyl) pyrrolidine (BPP) which (unsubstituted BPP) was one of the main side-products found in the solution polymerization of pyrrole.[16] It should be noted that the measured molecular weight depended on how long the sample was exposed to air on the trough surface or in THF solution. The M_w of the polymer from 3-decyl pyrrole was also slightly higher than that for the hexadecyl substituted one. However, it should be noted that the polystyrene calibration curve is perhaps a poor standard for the materials investigated as the polypyrrole backbone stiffens considerably at higher degrees of oxidation. The measured molecular weight while showing that a polymer was formed is therefore only indicative.

<Insert Figure 10 about here>

The transfer of monolayers onto solid substrates gave the following results. None of the compounds or their polymers could be transferred successfully onto hydrophilic substrates. Therefore, the substrates were hydrophobized. Monomer could be transferred successfully as monolayers from water onto hydrophobized substrates. Monolayers of monomer could be achieved only, since on subsequent dipping the layer was transferred back to the water surface. This behavior was independent of the surface pressure and dipping speed.

For the polymer the transfer was done directly from the subphase that was used for the polymerization. If acidic subphases were used, only a monolayer could be transferred onto hydrophobized substrates. The same was observed when the pH of the subphase was changed using ammonia. Therefore, polymerization was done with subphase solutions containing ammonium persulfate, only.

Transfer of more than monolayers of the polymerized monolayers was possible. The transfer ratio depended on the applied surface pressure while transferring and a uniform change in trough surface area with the amount of surface transferred.

The minimum required surface pressure for transfer was found to be above 25 mN/m. Best results were obtained with 35 to 40 mN/m. The barrier speed of about 1 to 3 mm/min and the dipper speed of about 1 to 10 mm/min had to be rather slow because the polymerized layer is highly viscous.

Under these conditions subsequent dipping allowed to built up Y-type multilayers as shown in Figure 10. As mentioned above, the partially oxidized polymer is not highly stable in air. Therefore, multilayer structures tended to degrade in air. A few minutes after the dipping, first holes in the multilayer film could be observed under the microscope.

Summary and Conclusions

3-Alkyl pyrroles could be polymerized at the air-water interface, yielding polymers that are expected to be highly regular ordered. The polymerization is possible without excess pyrrole in the subphase. The compounds were confirmed as polymers by NMR and GPC, however, no very high molecular weight compounds could be obtained. The reaction at the liquid-air interface could be monitored by changes in the surface area. Deposition of monolayers by Langmuir-Blodgett technique is possible and multilayers of the polymer can be prepared. The partially oxidized polymer multilayers tended to form pinholes.

Acknowledgments

The authors wish to acknowledge the Deutsche Forschungsgemeinschaft, the NSF sponsored REU site at the University of Florida, grant # CHE-9200344 for financial assistance for Mrs S. Keil and the ONR AASERT program for support of Mrs. C. Marestin.

References

1. McDiarmid, A.G.; Epstein A.J. *Lower-Dimensional Systems and Molecular Electronics*; Metzger, R. M.; et al. Eds. Plenum Press: New York, p. 303, 1991.
2. McDiarmid, A. G.; Yang, L. S.; Huang, W. S.; Humphrey,D. B. *Synth, Met.* 1987, *18*, 393.
3. Rühe, J.; Ezquerra, J. A.; Wegner, G. *Makromol. Chem. Rapid Commun.* 1989, *5*, 1.
4. Zhou, H. C.;Duran, R. S. *Thin Solid Films* 1992, *210/211*, 356.
5. Hong, K.; Rosner, R. B.; Rubner, M. F. *Chemistry of Materials* 1990, *2*, 82.
6. Rahman, A. K. M.; Samuelson, L.; Minehan, D.; Clough, S.; Tripathy, S.; Inagaki, T.; Yang, X. Q.; Skotheim, T. A.; Okamoto, Y. *Synth. Met.* 1989, *28*, C237.
7. Zhou, H.; Stern, R.; Batich, C.; Duran, R. S. *Makromol. Chem., Rapid Commun.* 1990, *11*, 409.
8. Bodalia, R. R.; Duran, R. S. *Polym. Prepr.* 1991, *32*, 248.
9. Gaines, G. L., Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience Publishers: New York, 1966.
10. Hong, K.; Rubner, M. F. *Thin Solid Films* 1988, *160*, 187.
11. Herrington, T. M.; Aston, M. S. *J. Colloid Interface Sci.* 1991, *141*, 50.
12. Yang, R.; Evans, D. F. *J. Phys. Chem.* 1990, *94*, 6117.

13. Zhou, H.; Duran, R. S. *Macromolecular Assemblies* ACS Symp. Ser. 493. Stroeve, P., Balazs, A. C., Eds.; ACS, Washington DC, 1992, p. 31

14. Wei, Y.; Sun, Y.; Tang, X. *J. Phys. Chem.* 1989, *93*, 4878.

15. Rühe, J. *thesis*, University of Mainz, 1989.

16. Rapi, S.; Bocchi, V.; Gardini, G. P. *Synth. Met.* 1988, *24*, 217.

FIGURE CAPTIONS

Figure 1 Chemical structures of (a) 3-decyl pyrrole, (b) 3-hexadecyl pyrrole and (c) 3-hexadecanoyl pyrrole

Figure 2 ^{1}H- and ^{13}C-NMR-spectra of (a) 3-hexadecyl pyrrole and (b) 3-hexadecanoyl pyrrole in CD_2Cl_2.

Figure 3 Isotherms of (a) 3-decyl pyrrole, (b) 3-hexadecyl pyrrole and (c) 3-hexadecanoyl pyrrole at an air-water interface, T = 23°C, subphase pure water, compression barrier speed = 50 mm/min.

Figure 4 Polymerization of 3-hexadecyl pyrrole. Subphase 0.05 M ferric chloride; temperature 23°C; surface pressure of polymerization constant at $\pi = 15$ mN/m.

Figure 5 Polymerization of 3-hexadecyl pyrrole. Subphase 0.03 M ammonium peroxodisulfate; temperature 23°C; surface pressure of polymerization constant at $\pi = 10$ mN/m.

Figure 6 Data from hysteresis experiments of the monolayer polymerization product of 3-hexadecyl pyrrole. Subphase 0.1 M sulfuric acid and 0.03 M ammonium persulfate, surface pressure of polymerization was constant at 20 mN/m. (a) expansion of the monolayer directly after polymerization; (b) first compression; (c) re-expansion; (d) recompression; (e) re-expansion.

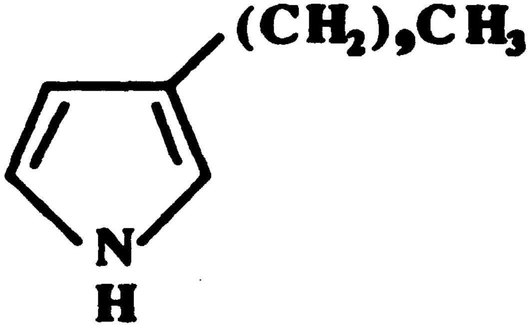
Figure 7 ^{1}H-NMR-spectrum of Langmuir monolayer polymerized 3-hexadecyl pyrrole and the suggested chemical structure.

Figure 8 IR-spectrum of (a) 3-hexadecyl pyrrole and (b) its monolayer polymerization product in KBr.

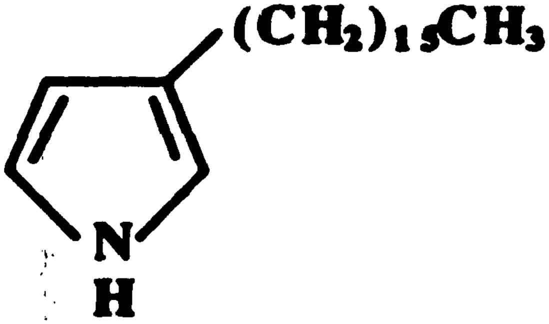
Figure 9 UV-vis spectra of (a) 3-hexadecyl pyrrole and (b) its polymerization product from the LB trough in chloroform solution.

Figure 10 Langmuir-Blodgett transfer of poly(3-hexadecyl pyrrole) onto hydrophobized glass. Transfer ratios for the dipping of 14 layers. Monolayer transferred from a diluted salt subphase (0.03 M ammonium persulfate).

A



B



C

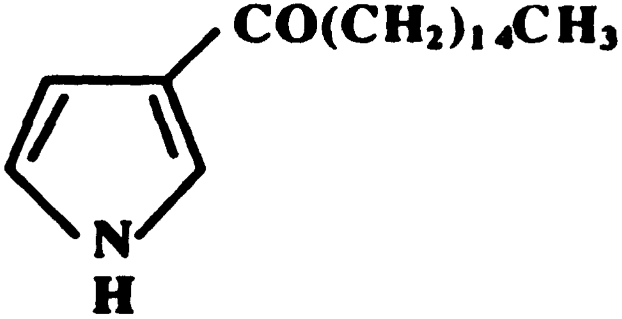
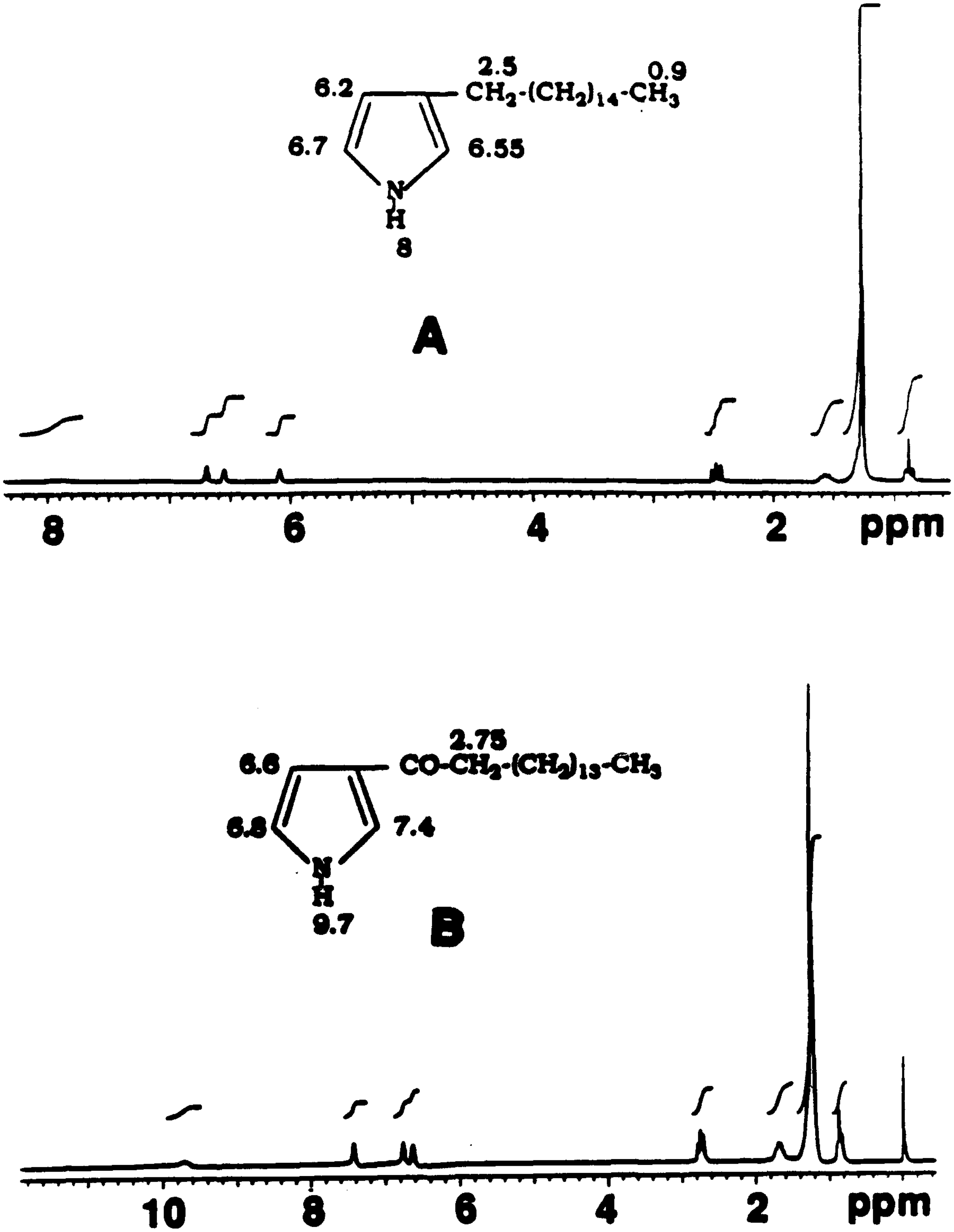
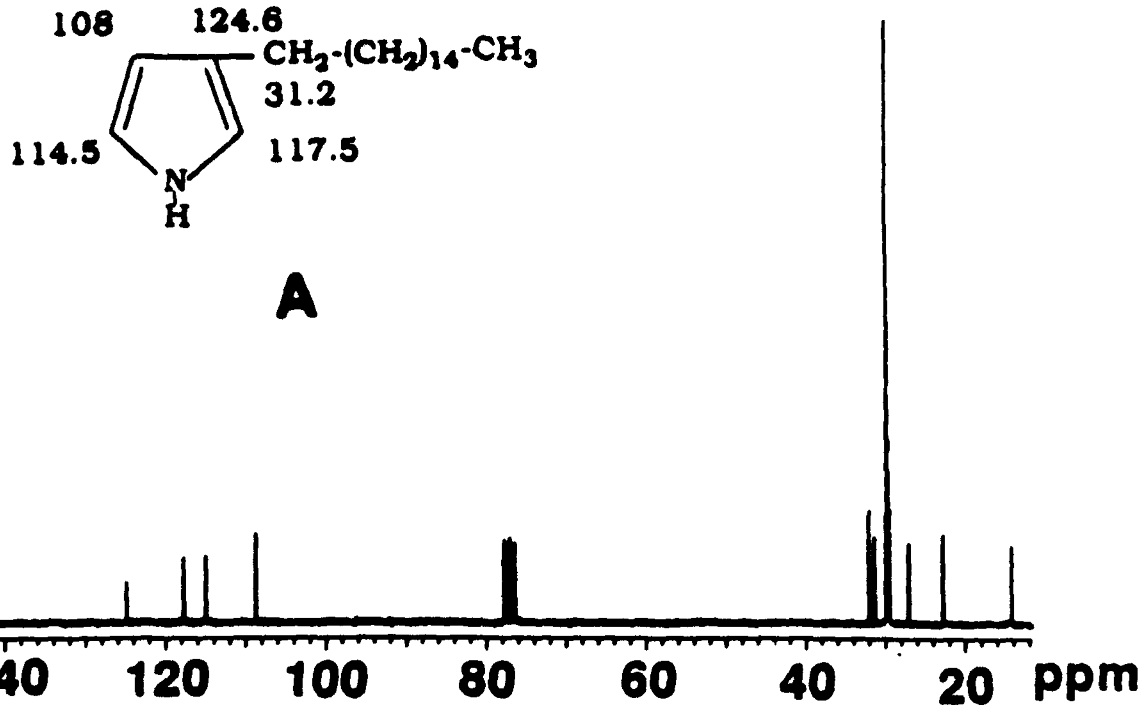


Fig II

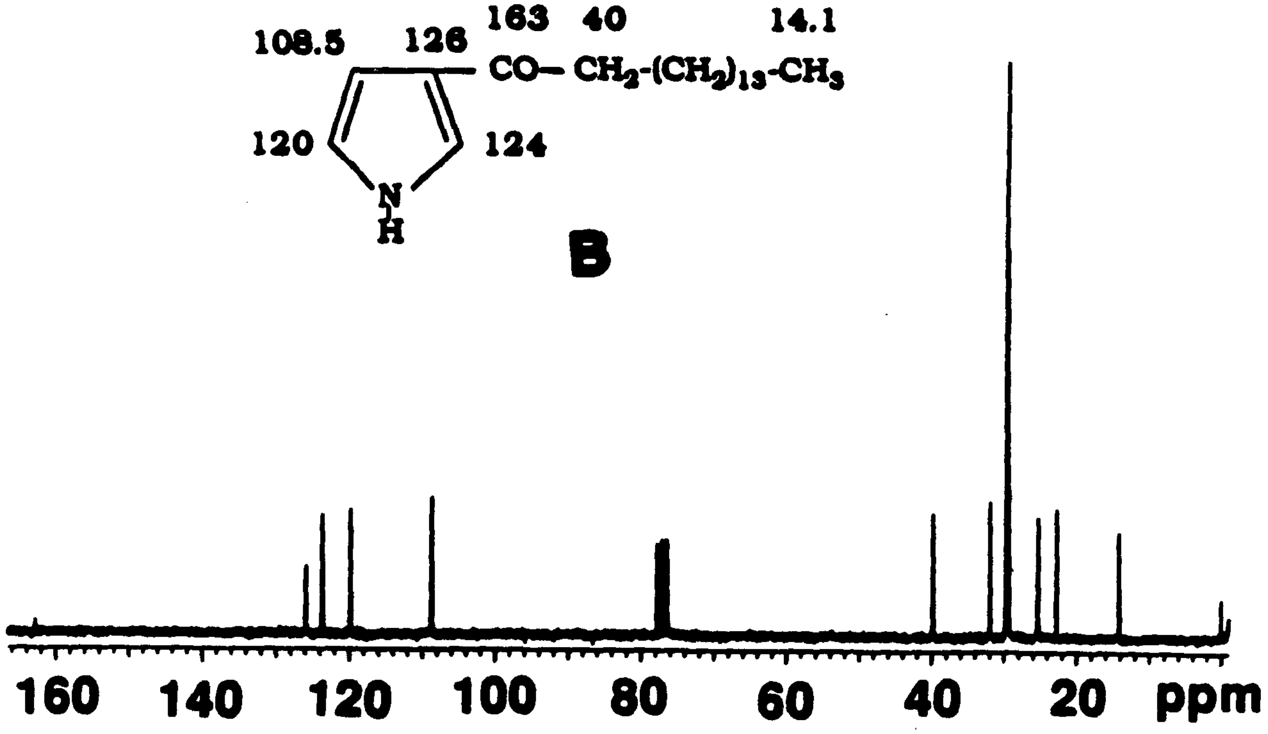


2.5
0.9
6.2
CH2-(CH2)14-CH3
6.7
6.55
N
H
8
A
8
6
4
2
ppm
2.75
6.6
CO-CH2-(CH2)13-CH3
6.8
7.4
N
H
9.7
B
10
8
6
4
2
ppm

Fig II


108
124.6
CH2-(CH2)14-CH3
31.2
114.5
117.5
N
H
160
140
120
100
80
60
40
20
ppm

A


163
40
14.1
108.5
126
CO– CH2-(CH2)13-CH3
120
124
N
H
160
140
120
100
80
60
40
20
ppm

B

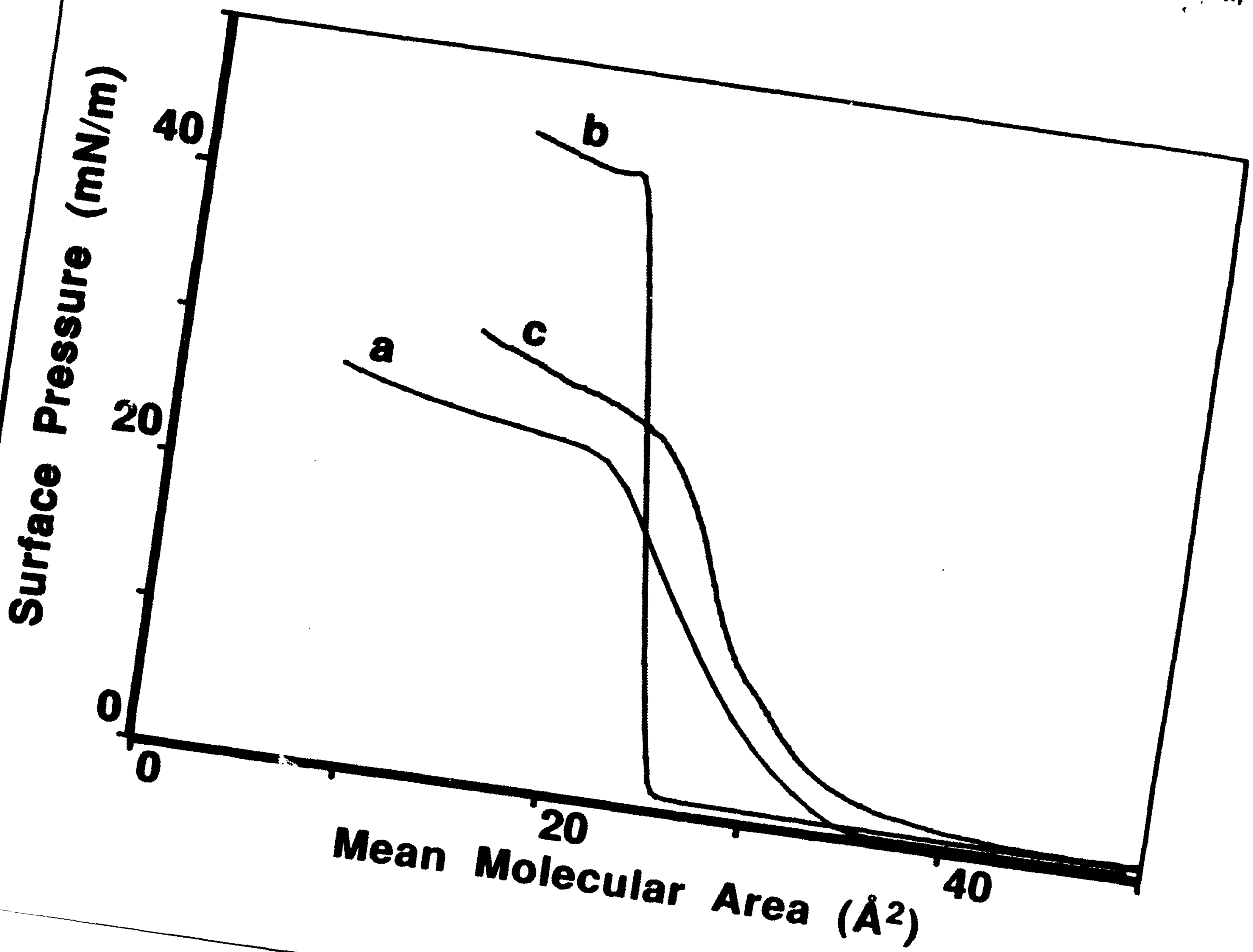

Surface Pressure (mN/m)
40
20
0
Mean Molecular Area (Å²)
0
20
40
a
b
c

Fig. IV

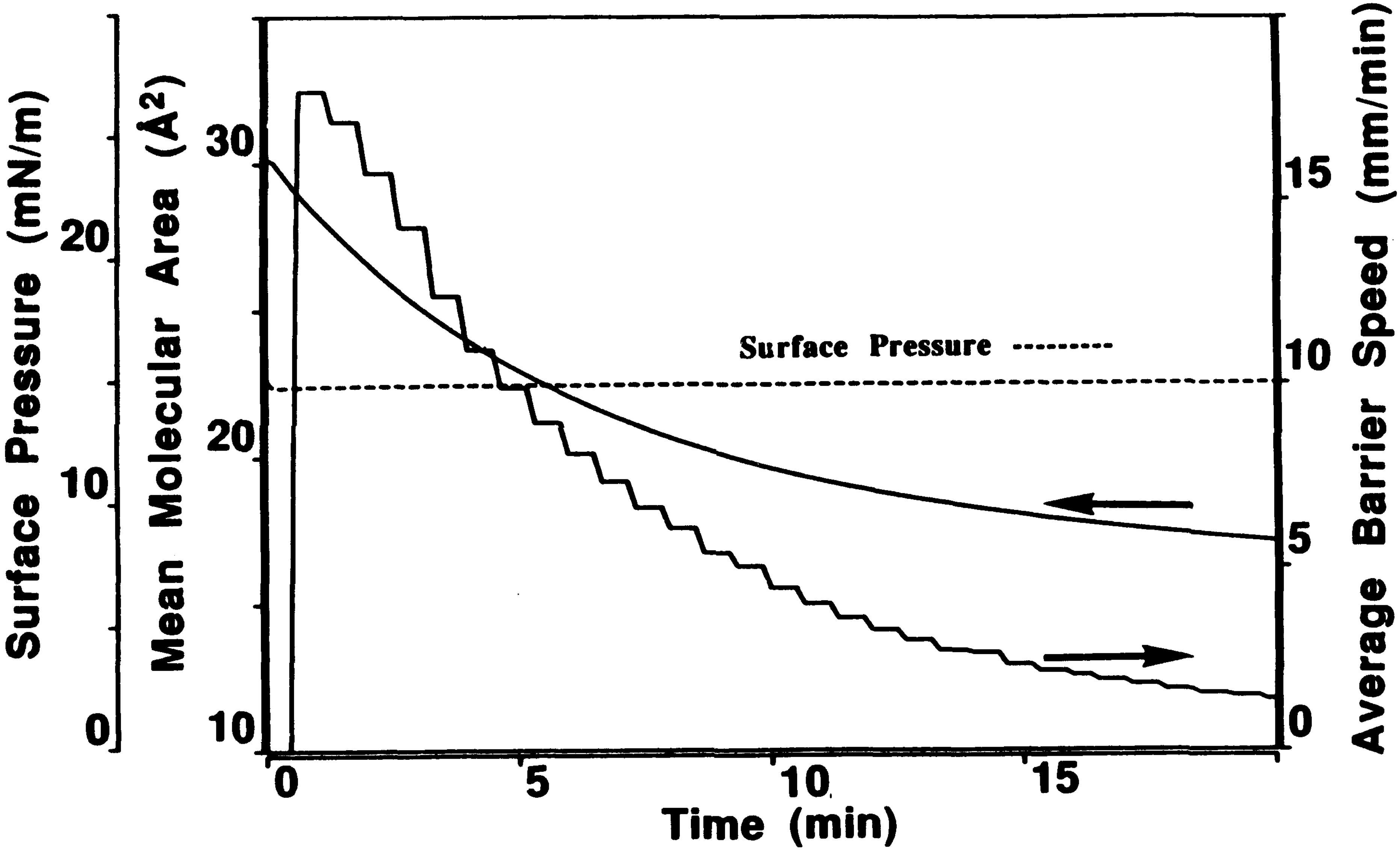

Surface Pressure (mN/m)
0
10
20
Mean Molecular Area (Å²)
10
20
30
Surface Pressure --------
Average Barrier Speed (mm/min)
0
5
10
15
Time (min)
0
5
10
15

Figure V

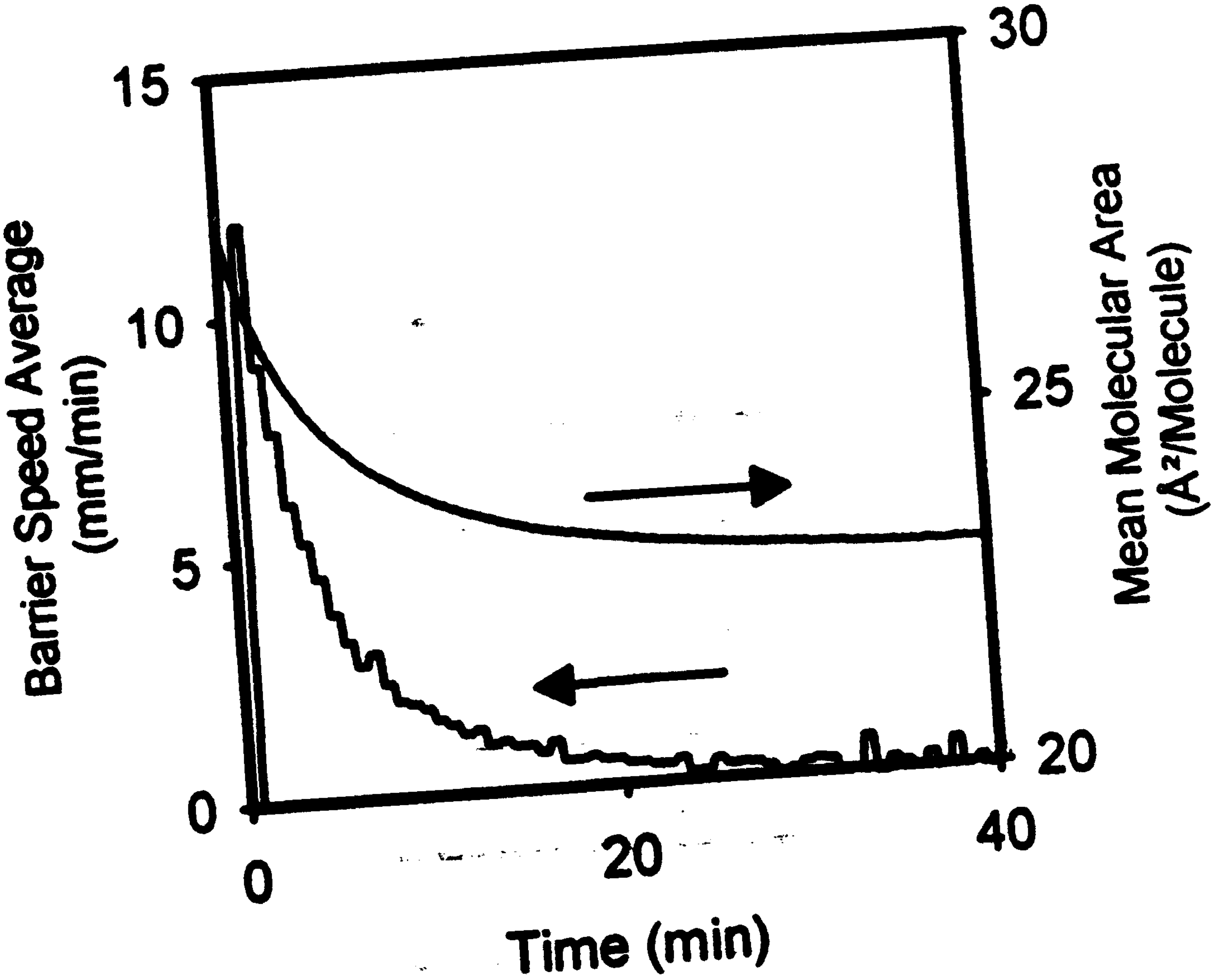
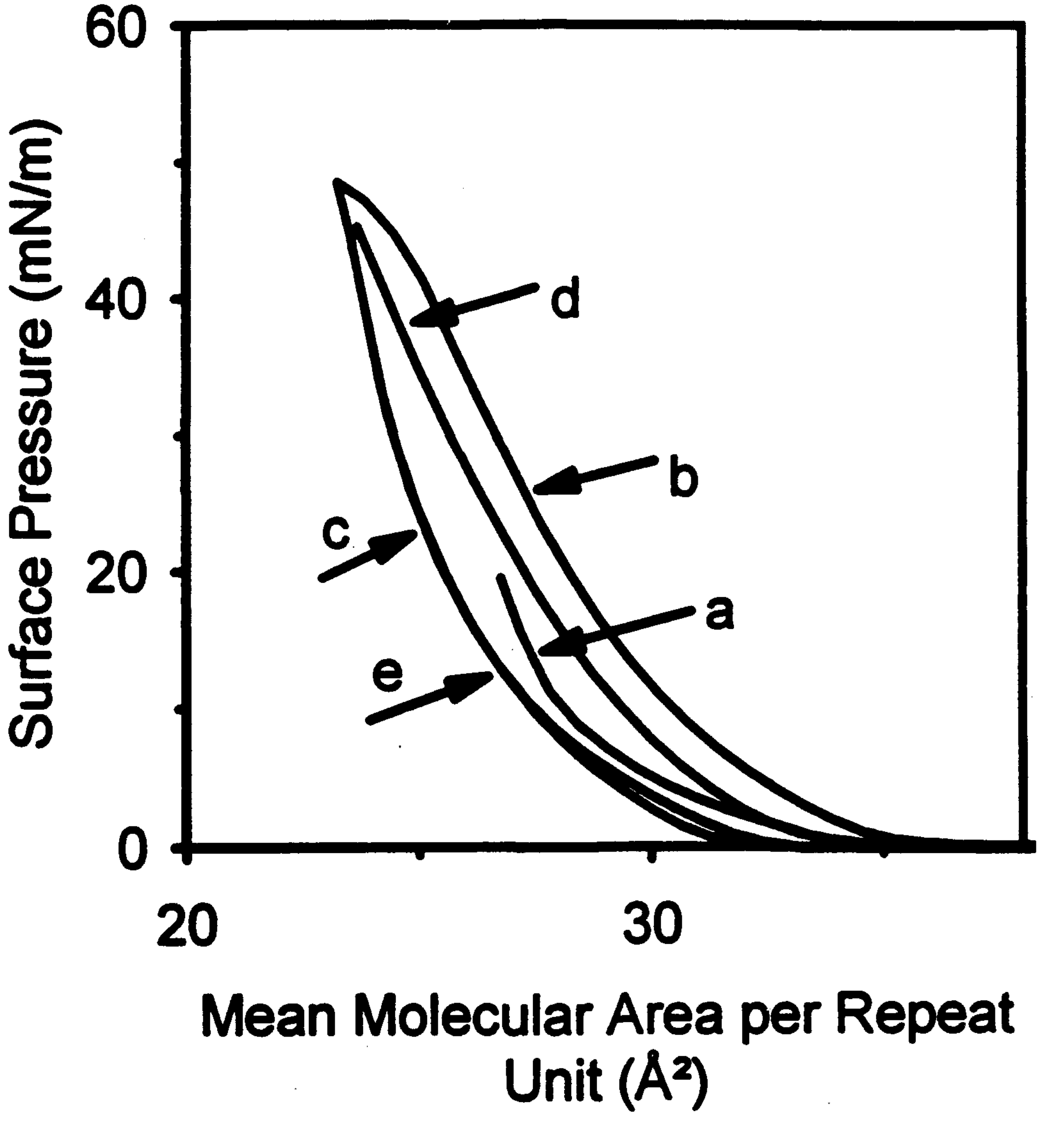

15
10
5
0
0
20
40
Time (min)
30
25
20
Barrier Speed Average (mm/min)
Mean Molecular Area (Å²/Molecule)

Figure 6



60
40
20
0
20
30
Surface Pressure (mN/m)
Mean Molecular Area per Repeat Unit (Å²)
a
b
c
d
e

Fig. 7

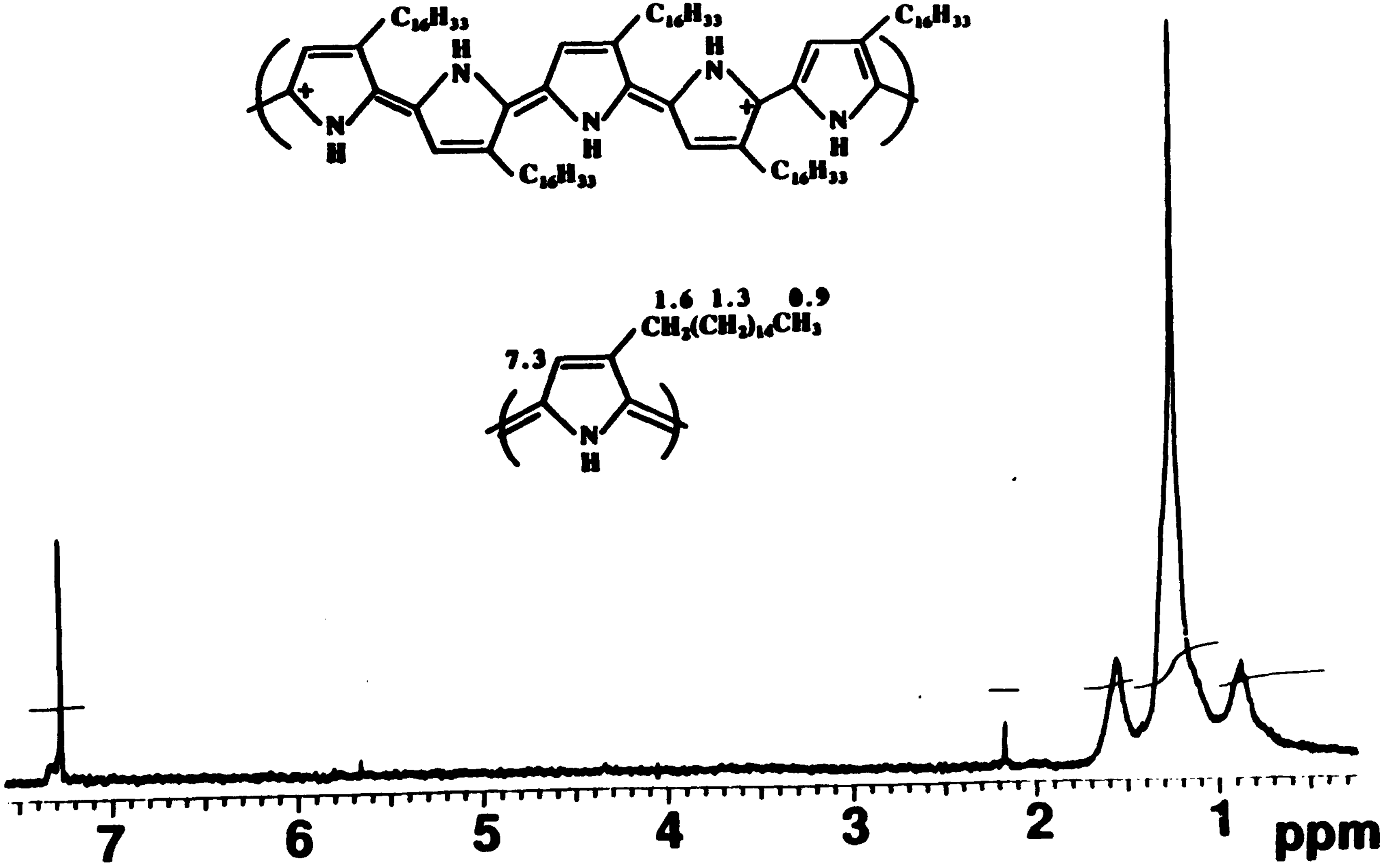

$C_{16}H_{33}$
$C_{16}H_{33}$
$C_{16}H_{33}$
$C_{16}H_{33}$
$C_{16}H_{33}$
N
H
+
1.6 1.3 0.9
$CH_2(CH_2)_{14}CH_3$
7.3
7
6
5
4
3
2
1
ppm

Fig. [illegible]

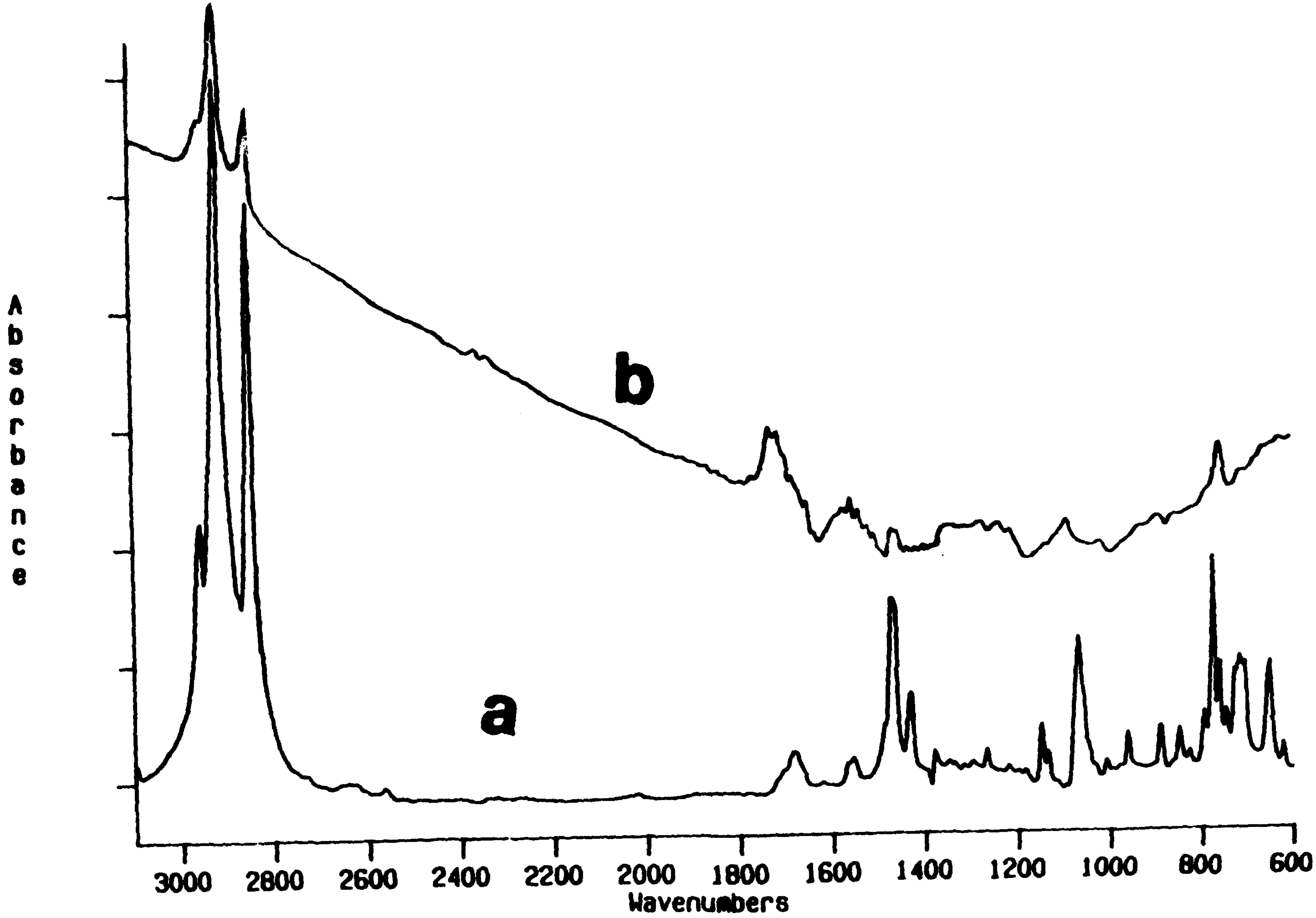

Absorbance
b
a
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Wavenumbers

Fig. 9

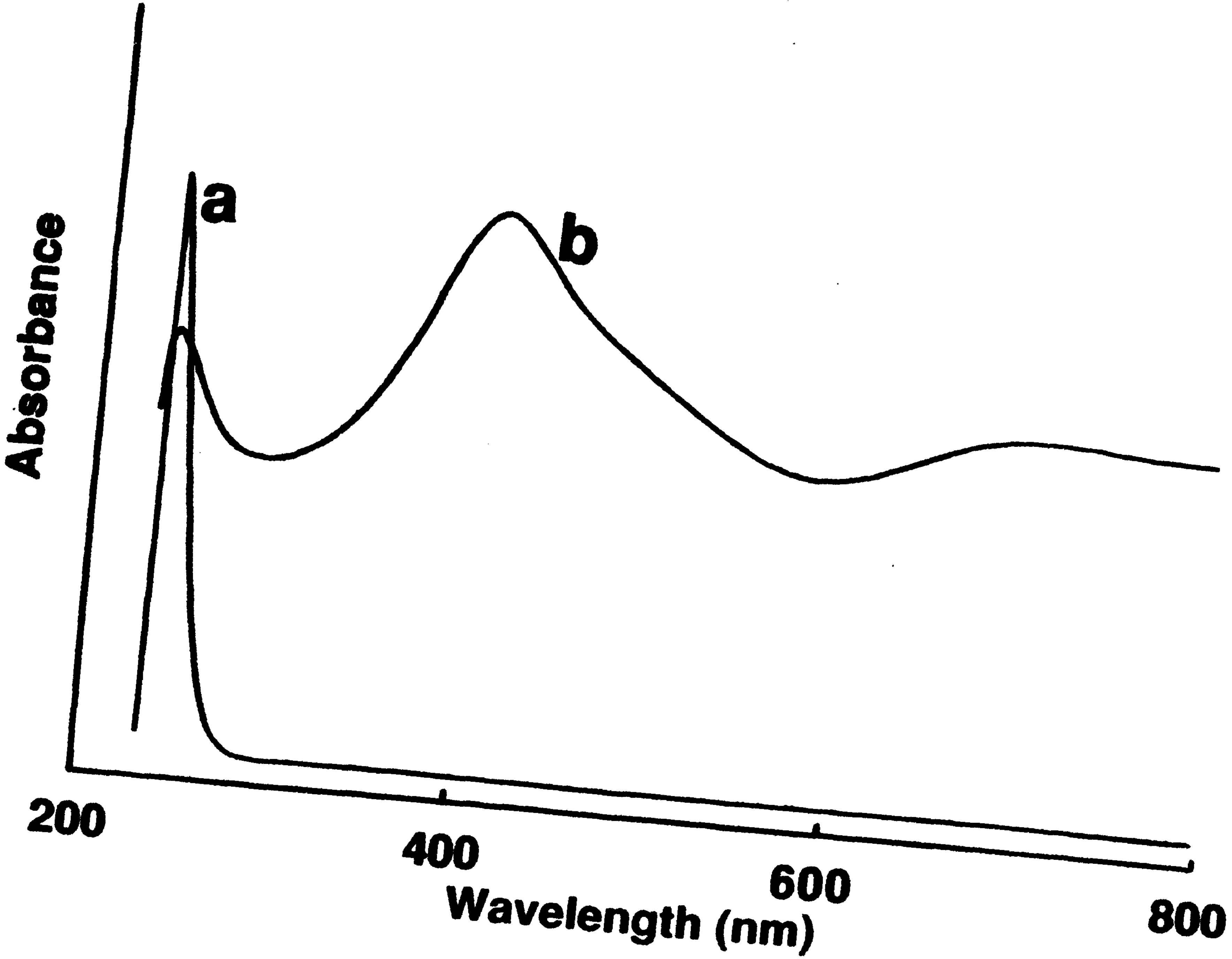
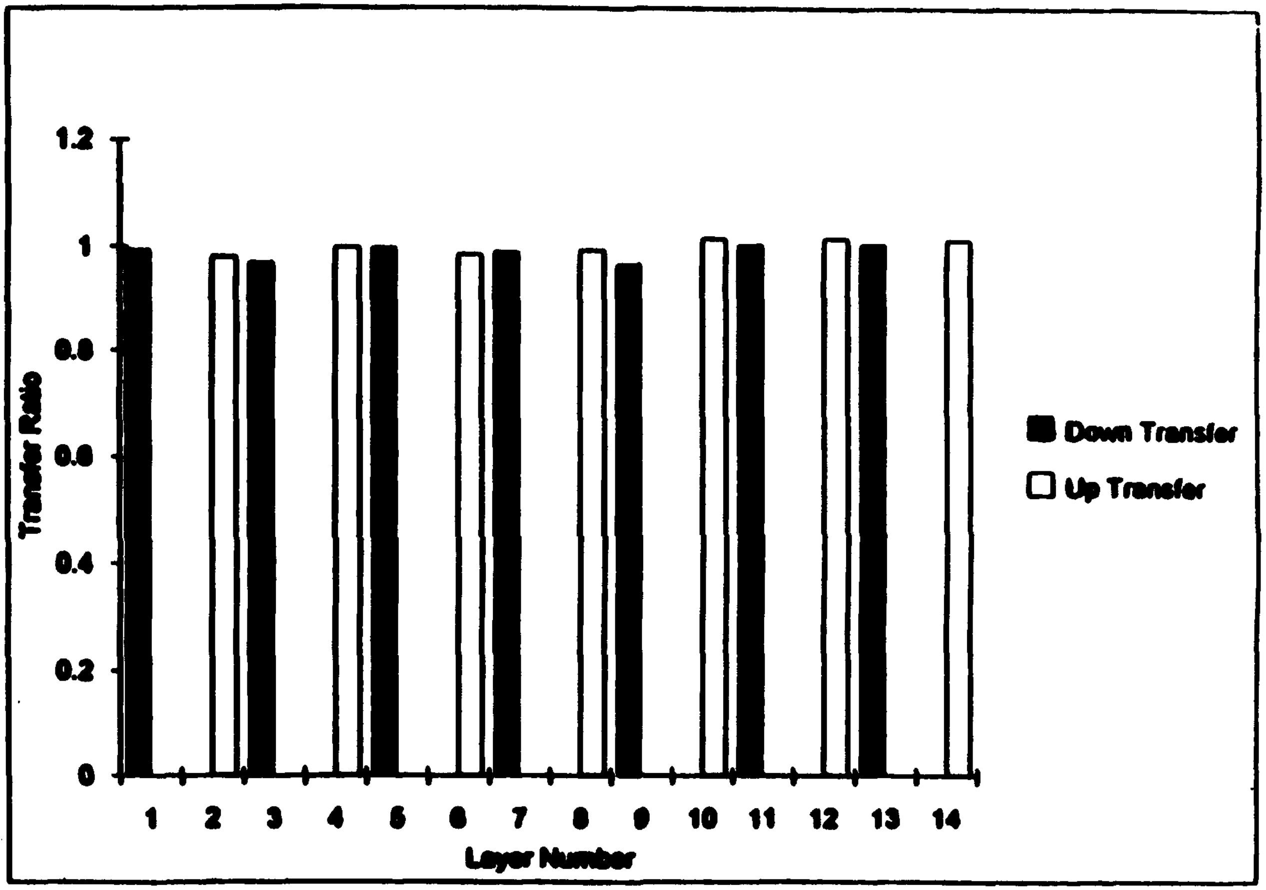


fig 10


1.2
1
0.8
0.6
0.4
0.2
0
Transfer Ratio
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Layer Number
■ Down Transfer
□ Up Transfer

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)*
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Weapons Center
China Lake, CA 93555-6001

Dr. Eugene C. Fischer (1)
Code 2840
David Taylor Research Center
Annapolis, MD 21402-5067

Dr. Elek Lindner (1)
Naval Ocean Systems Center
Code 52
San Diego, CA 92152-5000

Commanding Officer (1)
Naval Weapons Support Center
Dr. Bernard E. Douda
Crane, Indiana 47522-5050

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

Dr. Harold H. Singerman (1)
David Taylor Research Center
Code 283
Annapolis, MD 21402-5067

Chief of Naval Research (1)
Special Assistant for Marine
Corps Matters
Code 00MC
800 North Quincy Street
Arlington, VA 22217-5000

Defense Technical Information
Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

* Number of copies to forward

Enclosure