

Synthesis of Novel Electrically Conducting Polymers:
Potential Conducting Langmuir-Blodgett Films and Conducting
Polymers on Defined Surfaces.

51P

Final Report

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NOVEL ELECTRICALLY CONDUCTING
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Investigations Towards Electrically Conducting Langmuir-Blodgett Film; Thiophene-Based.

A. Introduction:

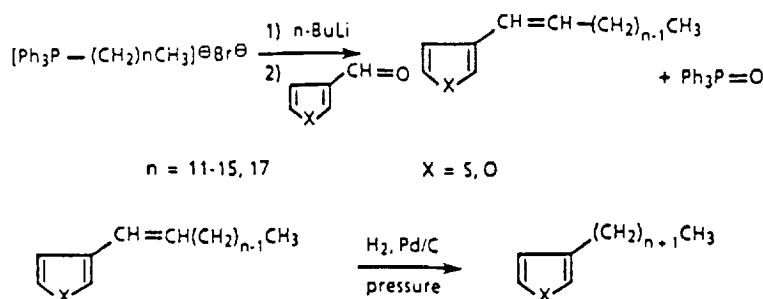
Based on previous results involving thiophene derived electrically conducting polymers in which we showed that thiophene, 3-substituted thiophenes, furans, and certain oligomers of these compounds showed electrical conductivity after polymerization. The conductivity was in the order of up to $500 \text{ S}\cdot\text{cm}^{-1}$. In addition, these polymers showed conductivity without being doped and most of all they were practically inert toward ambient conditions. They even could be used in aqueous media^{1,2,3}.

With these findings as a guide we synthesized a number of 3-long-chain-substituted thiophenes and 1-substituted-3-long-chain substituted pyrroles as monomers for potential polymeric electrically conducting Langmuir-Blodgett films.

Results; Synthesis:

The novel 3-long-chain substituted thiophenes and furans were synthesized by a Wittig reaction as outlined in Scheme 1.

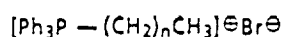
Scheme 1

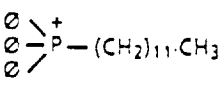
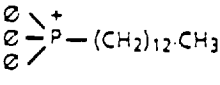
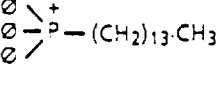
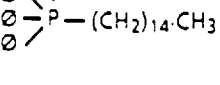
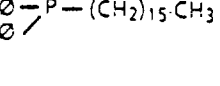
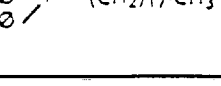


The needed alkyltriphenylphosphonium bromides were synthesized by reacting equal molar amounts of the appropriate alkylbromide with triphenylphosphane in refluxing acetonitrile.

In Table 1 (see next page), the synthesized alkyltriphenylphosphonium bromides are listed:

Table I



Alkyltriphenyl Phosphonium Bromides	M.P. °C	¹ H NMR (CDCl ₃) δ (ppm)	Yield %
	*	7.6-8.1 (m, 15H, aromatic protons) 3.7 (m, 2H, <u>CH₂</u> attached to P), 3.1 (dd, 2H, P- <u>CH₂CH₂</u>), 1.6 (bs, 4H, 2 <u>CH₂</u>), 1.2 (bs, 14H, 7 <u>CH₂</u>) 0.9 (t, 3H, <u>CH₃</u>)	60
	*	7.5-8.1 (m, 15H, aromatic protons), 3.75 (m, 2H, P- <u>CH₂</u>), 2.0 (bs, 2H, <u>CH₂CH₂</u>), 1.6-1.2 (bs, 20H, 10 <u>CH₂</u>) 0.9 (t, 3H, <u>CH₃</u>)	82
	52	7.5-8.1 (m, 15H, aromatic protons), 3.7 (m, 2H, P- <u>CH₂</u>), 1.9 (bs, 2H, <u>CH₂CH₂</u>) 1.65-1.2 (bs, 2 bs, 22H, 11 <u>CH₂</u>) 0.9 (t, 3H, <u>CH₃</u>)	80
	53-4	7.6-8.1 (m, 15H, aromatic protons) 3.8 (m, 2H, P- <u>CH₂</u>), 1.7-1.2 (bs, 2 bs, 26H, 13 <u>CH₂</u>), 0.9 (t, 3H, <u>CH₃</u>)	84
	*	7.6-8.1 (m, 15H, aromatic protons) 3.7 (m, 2H, P- <u>CH₂</u>), 1.7 and 1.25 (2 bs, 28H, 14 <u>CH₂</u>) 0.9 (t, 3H, <u>CH₃</u>)	68
	101	7.6-8.1 (m, 15H, aromatic protons) 3.8 (b, 2H, P- <u>CH₂</u>) 2.0-1.45 (b, 6H, 3 <u>CH₂</u>) 1.2 (2 bs, 26H, 13 <u>CH₂</u>) 0.9 (t, 3H, <u>CH₃</u>)	88

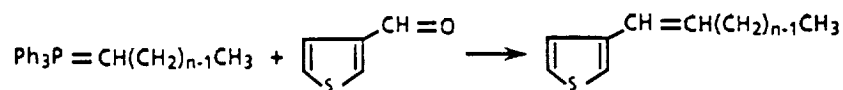
*non-crystalline wax-like solids







These phosphonium bromides after dissolving in tetrahydrofuran were deprotonated to the ylide by adding an equal molar amount of n-butyl lithium. After a short time thiophene-3-carbaldehyde or furan-3-carbaldehyde resp was added. After standing overnight the reaction mixture was quenched with an

aqueous sodium chloride solution. Purification was achieved by column chromatography.

In Tables II and III the synthesized 3-(alk-1-en-1-yl) thiophenes and 3-(alk-1-en-yl) furans are listed.

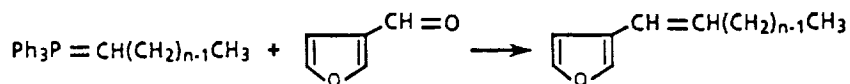
Table II







3-(Alk-1-en-1-yl)thiophene	M.P	¹ H NMR (CDCl ₃) δ (ppm)	Elemental Analyses		λ _{max} (nm) CHCl ₃	Yield %
			Calcd. Found	C, H C, H		
 CH = CH(CH ₂) ₁₀ -CH ₃	*	7.2 (m, 3H, ring protons) 6.3 and 5.6 (2m, 2H, -CH = CH) 2.3 and 1.4 (m, bs, 20H, 10 CH ₂), 0.9 (t, 3H, CH ₃)	77.21 77.40	10.67 10.63	249	58
 CH = CH(CH ₂) ₁₁ -CH ₃	*	7.2 (m, 3H, ring protons), 6.3 and 5.6 (2m, 2H, CH = CH) 2.3 and 1.4 (2bs, 22H, 11 CH ₂), 0.9 (t, 3H, CH ₃)	77.63 77.50	10.86 10.67	251	61
 CH = CH(CH ₂) ₁₂ -CH ₃	*	7.2 (m, 3H, ring protons), 6.3 and 5.6 (2m, 2H, CH = CH) 2.3 and 1.4 (2bs, 24H, 12 CH ₂) 0.9 (t, 3H, CH ₃)	78.01 77.81	11.03 10.86	250	58
 CH = CH(CH ₂) ₁₃ -CH ₃	*	7.0-7.3 (m, 3H, ring protons), 6.3 and 5.6 (2m, 2H, CH = CH) 2.2 and 1.35 (2 bs, 26H, 13 CH ₂), 0.9 (t, 3H, CH ₃)	78.36 78.12	11.18 11.07	250	56
 CH = CH(CH ₂) ₁₄ -CH ₃	45	7.0-7.3 (m, 3H, ring protons), 6.4 and 5.7 (2m, 2H, CH = CH), 3.5 (m, 2H, CH ₂ attached to olefinic C), 1.5 (bs, 26H, 13 CH ₂), 0.9 (t, 3H, CH ₃)	78.68 78.66	11.32 11.44	249	75
 CH = CH(CH ₂) ₁₆ -CH ₃	40-1	7.2 (m, 3H, ring protons) 6.4 and 5.65 (2m, 2H, CH = CH), 2.2 and 1.4 (2bs, 32H, 16 CH ₂), 0.85 (t, 3H, CH ₃)	79.24 79.48	11.56 11.29	249	49

*non-crystalline wax-like solids

Table III

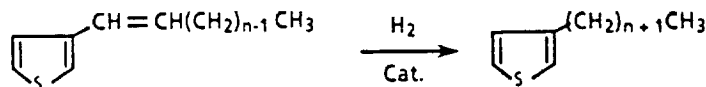








3(-Alk-1-en-1-yl)-furan	M.P. °C	¹ H NMR (CDCl ₃) δ (ppm)	Elemental Analyses		λ _{max} (nm) CHCl ₃	Yield %
			Calcd. C, H	Found C, H		
 $\text{CH} = \text{CH}(\text{CH}_2)_{11}\text{CH}_3$	*	7.4 (m, 2H, position 2 and 5 in furan ring), 6.45 (bs, 1H, position 4 in furan), 6.15 and 5.6 (2m, 2H, CH = CH), 2.15 (bs, 4H, 2 CH_2), 1.4 (bs, 18H, 9 CH_2), 0.9 (t, 3H, CH_3)	82.38 82.18	11.52 11.63	247	36
 $\text{CH} = \text{CH}(\text{CH}_2)_{13}\text{CH}_3$	38	7.4 (m, 2H, position 2 and 5 in furan ring), 6.45 (bs, 1H, position 4 in furan ring), 6.15 and 5.6 (2m, 2H, -CH = CH-), 2.15 (bs, 4H, 2 CH_2), 1.3 (bs, 22H, 11 CH_2), 0.9 (t, 3H, CH_3)	82.69 82.48	11.80 11.64	245	39
 $\text{CH} = \text{CH}(\text{CH}_2)_{14}\text{CH}_3$	48	7.4 (m, 2H, position 2 and 5 in furan ring), 6.45 (bs, 1H, position 4 in furan ring), 6.15 and 5.6 (2m, 2H, -CH = CH-), 2.2 (bs, 4H, 2 CH_2), 1.3 (bs, 24H, 12 CH_2), 0.9 (t, 3H, CH_3)	82.83 83.00	11.92 11.76	244	33
 $\text{CH} = \text{CH}(\text{CH}_2)_{16}\text{CH}_3$	50	7.4 (m, 2H, position 2 and 5 in furan ring), 6.45 (bs, 1H, position 4 in furan ring), 6.15 and 5.6 (2m, 2H, -CH = CH-), 2.2 (bs, 4H, 2 CH_2), 1.3 (bs, 28H, 14 CH_2), 0.9 (t, 3H, CH_3)	83.06 83.07	12.12 11.90	248	81

*non-crystalline wax-like solids

The desired 3-long-chain alkylthiophenes and furans resp. were obtained in good to very good yields by hydrogenation in the presence of a Pd/C catalyst. The results are presented in Tables IV and V.

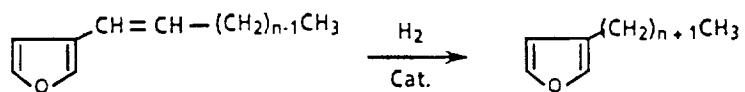
Table IV

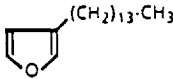
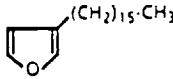
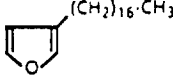
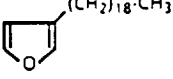


Reduction Products [3-Alkylthiophene]	M.P. °C	¹ H NMR (CDCl ₃) δ (ppm)	Elemental Analyses		λ _{max} (nm) CHCl ₃	Yield %
			Calcd. Found	C, H C, H		
 (CH ₂) ₂ -CH ₃	*	7.2 (dd, 1H, in position 5 of the thiophene ring), 6.9 (d, 2H, in position 2 and 4 in the thiophene ring), 2.6 (t, 2H, <u>CH</u> ₂ attached to thiophene ring), 2.3 (bs, 22H, 11 <u>CH</u> ₂), 0.9 (t, 3H, <u>CH</u> ₃)	76.62 76.42	11.35 11.63	244	83
 (CH ₂) ₃ -CH ₃	*	7.2 (dd, 1H, 5 position in thiophene ring), 6.2 (d, 2H, in position 2 and 4 thiophene ring), 2.6 (t, 2H, <u>CH</u> ₂ attached to thiophene ring), 2 and 1.3 (2bs, 24H, 12 <u>CH</u> ₂), 0.9 (t, 3H, <u>CH</u> ₃)	77.07 77.04	11.50 11.32	244	86
 (CH ₂) ₄ -CH ₃	*	7.2, 6.9 (2m, 3H, thiophene ring), 2.6 (t, 2H, <u>CH</u> ₂ attached to thiophene ring), 1.7, 1.3 (2bs, 26H, 13 <u>CH</u> ₂), 0.9 (t, 3H, <u>CH</u> ₃)	77.48 77.56	11.63 11.60	245	68
 (CH ₂) ₅ -CH ₃	*	7.25 and 6.9 (2m, 3H, thiophene ring), 2.6 (t, 2H, <u>CH</u> ₂ attached to thiophene ring), 1.2 and 1.3 (2bs, 28H, 14 <u>CH</u> ₂), 0.9 (t, 3H, <u>CH</u> ₃)	77.85 77.60	11.76 11.67	244	72
 (CH ₂) ₆ -CH ₃	30	7.2 and 6.9 (2m, 3H, thiophene ring), 2.6 (t, 2H, <u>CH</u> ₂ attached to thiophene ring), 1.3 (2bs, 30H, 15 <u>CH</u> ₂), 0.9 (t, 3H, <u>CH</u> ₃)	78.19 78.37	11.87 11.64	244	50
 (CH ₂) ₈ -CH ₃	43	7.2 and 6.9 (2m, 3H, thiophene ring), 2.6 (diffuse t, 2H, <u>CH</u> ₂ attached to the thiophene ring), 1.2 (bs, 34H, 17 <u>CH</u> ₂), 0.9 (t, 3H, <u>CH</u> ₃)	78.78 78.90	12.07 12.07	242	64

*non-crystalline wax-like solids

Table V



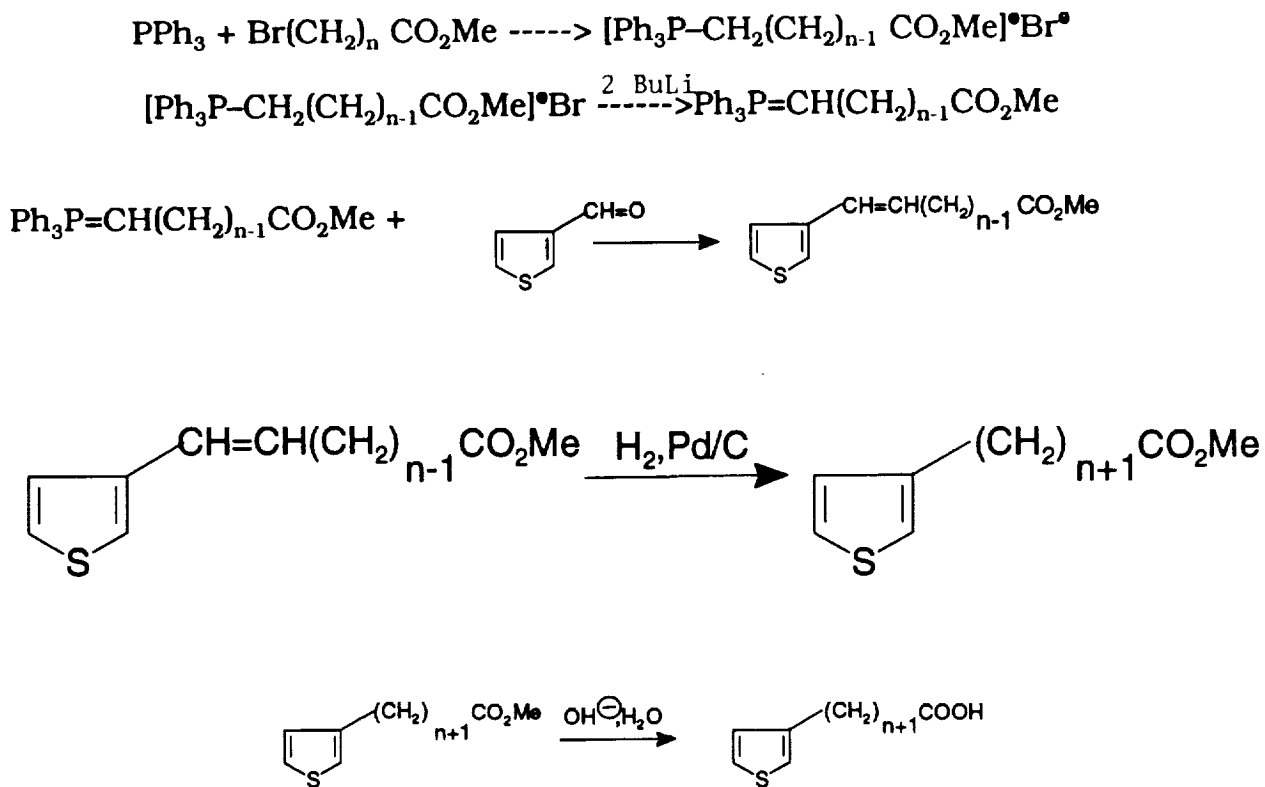
Reduction Products [3-Alkylfuran]	M.P. °C	¹ H NMR (CDCl ₃) δ (ppm)	Elemental Analyses		λ _{max} (nm) CHCl ₃	Yield %
			Calcd. Found	C H		
	*	7.35 and 7.2 (2bs, 2H, in 2 and 5 position in furan ring), 6.2 (bs, 1H, in position 4 in furan ring), 2.35 (t, 2H, <u>CH₂</u> attached to furan ring), 1.30 (s, 24H, 12 <u>CH₂</u>), 0.9 (t, 3H, <u>CH₃</u>)	81.75 81.99	12.19 11.66	244	80
	*	7.35 and 7.20 (2bs, 2H, position 2 and 5 in furan ring), 6.25 (bs, 1H, in position 4 in furan ring), 2.4 (t, 2H, <u>CH₂</u> attached to furan ring), 1.3 (s, 28H, 14 <u>CH₂</u>), 0.9 (t, 3H, <u>CH₃</u>)	88.12 81.93	12.41 12.70	244	83
	*	7.35 and 7.20 (2bs, 2H, in position 2 and 5 in furan ring), 6.25 (bs, 1H, in position 4 in furan ring), 2.4 (t, 2H, <u>CH₂</u> attached to furan ring), 1.35 (s, 30H, 15 <u>CH₂</u>), 0.9 (t, 3H, <u>CH₃</u>)	82.28 82.43	12.50 12.31	244	90
	*	7.35 and 7.2 (2bs, 2H, in position 2 and 5 in furan ring), 6.25 (bs, 1H, in position 4 in furan ring), 2.4 (t, 2H, <u>CH₂</u> attached to furan ring), 1.3 (s, 34H, 17 <u>CH₂</u>), 0.9 (t, 3H, <u>CH₃</u>)	82.57 82.32	12.65 12.56	243	85

* non-crystalline wax-like solids

ω -3-Thienyl-long-chain carboxylic acids:

Three of such acids were prepared. This synthesis was achieved also by a Wittig reaction followed by hydrogenation of the corresponding unsaturated ester with subsequent hydrolysis (Scheme II).

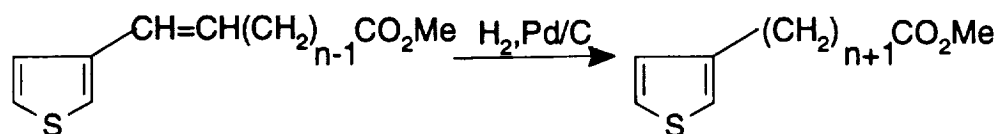
Scheme II:



$$n = 7, 11, 15$$

The results of the synthesis of esters are compiled in Table VI. The acids were obtained by alkaline hydrolysis of the esters and identified by $^1\text{HNMR}$.

Table VI



n	C calcd % C found	H calcd H found
6	66.10 65.43	8.72 8.95
10	70.08 69.89	9.15 9.24
14*		

identified by MS and $^1\text{H-NMR}$.

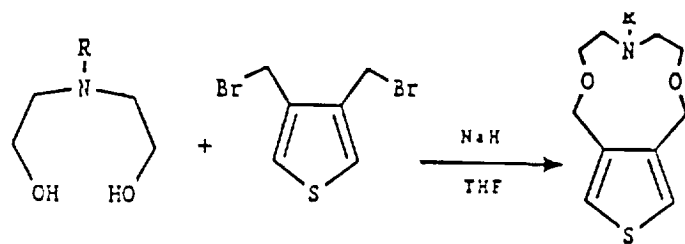
As a result of the collaboration with Professor J. Lando at Case-Western Reserve University, a number of novel crown ethers with a long-side chain were thought to be potentially good candidates as monomers for conducting Langmuir-Blodgett Films.

The synthesis was planned to proceed as indicated in Schemes III, IV, V and VI. The target compound was the N-stearyl derivative. As a model compound for this synthesis we prepared the N-ethyl derivative. This compound was obtained in good yield according to the outlined reaction sequence.

To achieve the preparation of the desired compound it was planned to synthesize the N-benzyl compound. After hydrogenolysis of the benzyl group, a routine reaction, the free amino compound should be reacted with stearyl chloride to give the desired long-chain species. However, completely unexpectedly the hydrogenolysis did not work.

Further attempts toward this highly desirable and potentially useful compound were abandoned due to termination of the grant.

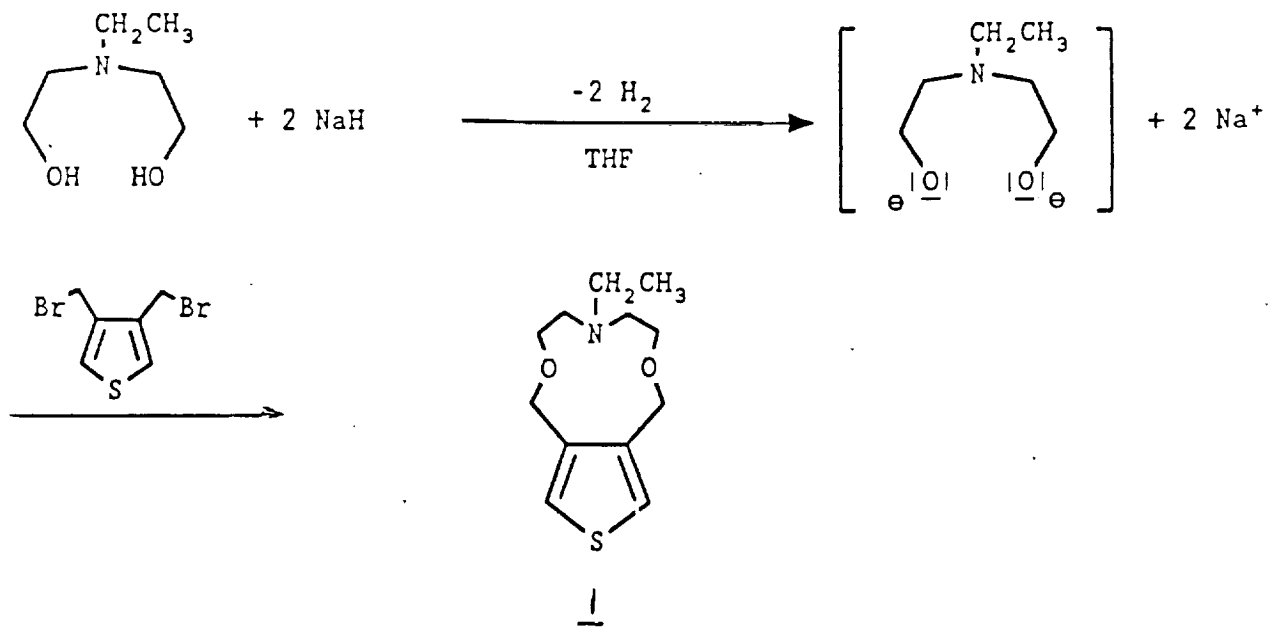
Scheme III



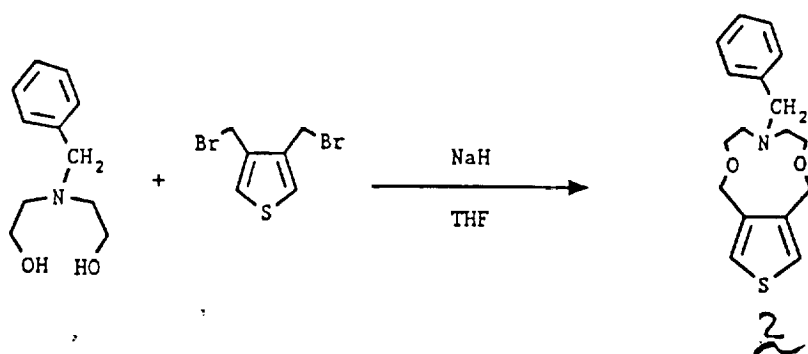
R - Ethyl
 - Benzyl
 - Stearyl

R-H
 - Ethyl
 - Stearyl

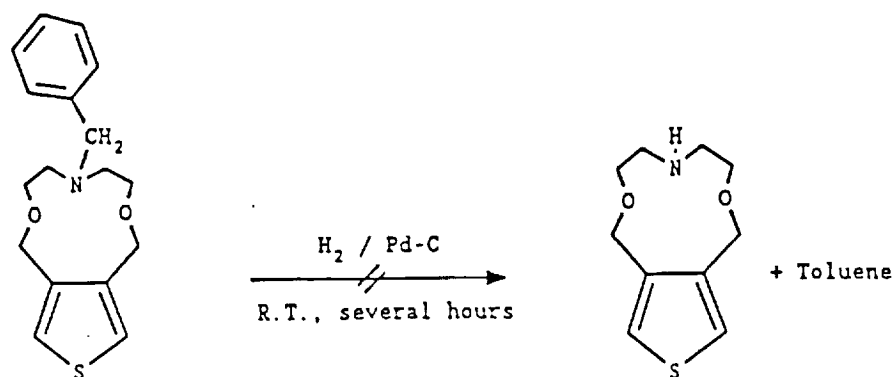
Scheme IV



Scheme V



Scheme VI



Experimental:

General procedure for the preparation of ω -alkyltriphenylphosphonium bromides. The following procedure for the reaction of 1-bromododecane with triphenylphosphine is generally representative for the preparation of phosphonium salts (Table I).

A mixture of 1-bromododecane (7.72 g, 39 mm), triphenylphosphane (11.8 g., 45 mm) and acetonitrile (150 ml) was stirred magnetically and heated under N_2 . After 36 h reflux time the solvent was evaporated on a rotary evaporator under reduced pressure. The residue which was a mixture of ω -alkyltriphenylphosphonium bromide and triphenylphosphane was purified by using a silica gel column. The mobile phase was first petroleum ether (37-59°C) and then diethyl ether. The phosphonium salt was eluted from the silica gel column by methanol. Evaporation of methanol gave 12 g of solid material (yield 60.15%).

3-(Alk-1-en-1-yl)thiophenes. The preparation of 3-(dodeca-1-en-1-yl)thiophene represents a typical example for the alkenes. In a three necked nitrogen flushed, round-bottomed flask fitted with magnetic stirrer and septum, the phosphonium bromide derived from 1-bromododecane (5.25 g, 12.18 mm) in dry THF (50 ml) was stirred magnetically under N_2 , and cooled (ca. 5° C) in an ice bath. *n*-BuLi (1.6M in hexane) (7.6 ml, 12.18 mm) was added dropwise by means of a syringe. The color of the reaction mixture changed to violet and then to orange-red. After 20 minutes, 1.12 g (10 mm) of 3-thiophenecarboxaldehyde in 10 ml THF was added slowly whereby the color of the reaction mixture turned from pale yellow to light brown. After removing the ice bath, stirring continued overnight. Workup was done by pouring the reaction mixture on conc. NaCl solution followed by extraction with diethyl ether. After drying over anhydrous $MgSO_4$, and distilling off the solvent, the material was purified by chromatography using a silica gel column and petroleum ether (37-59°C) as eluent to give 1.55 g of material (58.7%) (Table II).

3-(Alk-1-en-1-yl)furans. Preparation analogously to the thiophene derivatives (Table IV).

Synthesis of 3-alkylthiophenes. The reduction of an olefinic thiophene is presented as an example for all other reductions.

A solution of 3-(stearyl-1-en-1-yl) thiophene (2.044 g, 3 mm) in ethyl acetate (50 ml) was hydrogenated in the presence of 5% Pd/C (500 mg) as a catalyst for six h under 40 lbs/sq. inch of H_2 -pressure. The mixture was filtered and the solvent removed. The product was purified by column chromatography using silica gel and petroleum ether (37-59°C) as eluent to give 0.87 g of material (65.5%) (Table III).

3-Alkyfurans. The preparation of the 3-alkylfurans was performed in the same manner as described above, except that the pressure used was only 20 lbs/sq. inch (Table V).

Synthesis of 6-ethyl-6-aza-3, 9-dioxa-14-thiabicyclo-[9,3,0]pentadeca-1(15),12-diene, 1.

To a slurry consisting of 0.528 g of NaH as 60% suspension in mineral oil and 0.317 g N-ethyl-diethanolamine in THF was added 1 g. of 3,4-bis(bromomethyl) thiophene. After refluxing for 20 hours (monitored by TLC for disappearance of starting material) the mixture was carefully quenched with ice water (NaH!). The THF was distilled off and the remainder was extracted with ether and the ether extract was dried over anhyd magnesium sulfate. After evaporating the ether final purification was achieved by column chromatography. A yield of 77% of a yellow oil was obtained.

Elemental Analysis (M, W, 241.4) Ccalc. 59.72%.
C found 59.56%; H calc. 7.94%; H found 7.90%.

Synthesis of 6-benzyl-6-aza-3,9-dioxa-14-thiabicyclo [9,3,0]pentadeca-1(15,12-diene).

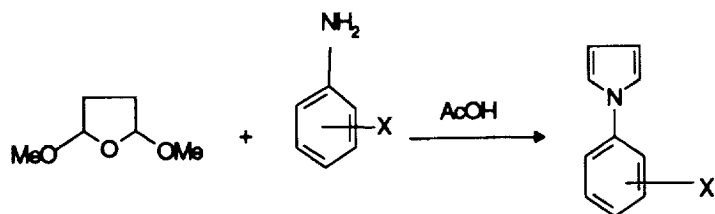
This compound was synthesized similar to 1 from N-benzyl-diethanolamine and obtained as a light yellow oil in 42% yield. Elemental analysis calculated for $C_{17}H_{21}NO_2S$.

C cal. 67.29%; C found 67.20%; H calc 6.89%; H found 6.84%.

N-Substituted-3-Long-Chain-Substituted Pyrroles as Monomers for Potential Electrically Conducting Langmuir Blodgett Films.

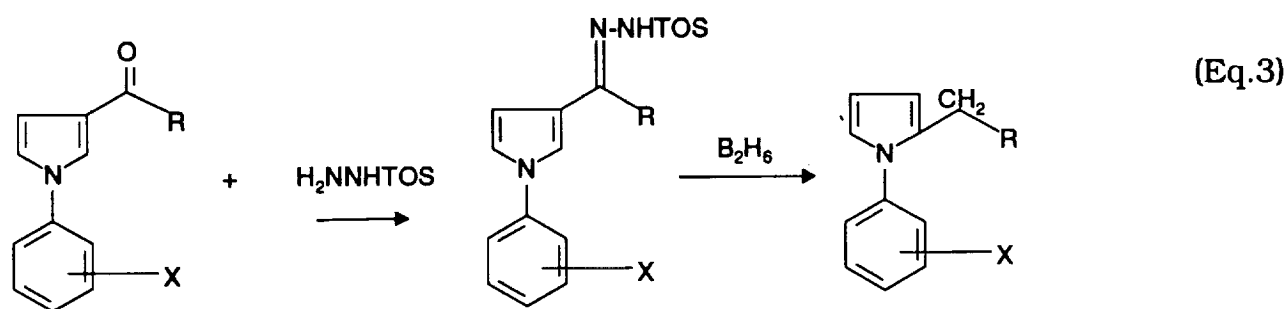
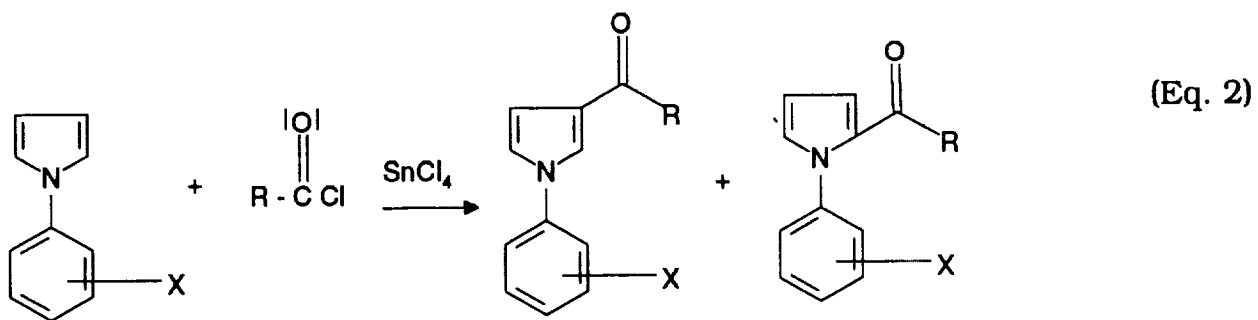
The synthesis of the desired pyrroles was accomplished by the following sequence of reaction (Scheme VII).

Scheme VII



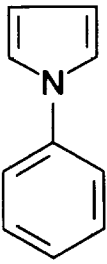
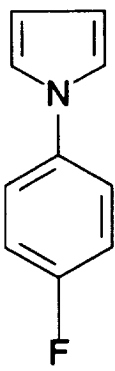
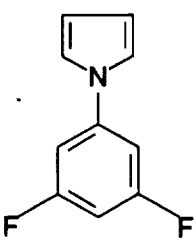
(Eq. 1)

X=H, F, 3,5-F



The N-substituted pyrroles prepared according to Equation 1 are listed in Table VII.

Table VII

Product	mp°C	(M _s)	¹ H NMR(CDCl ₃)S(PPM)	Yield
	56-57°C Lit (57-60°C)	(MW:143.2) 143.05 100%	7.39 and 7.26 (2M, 5H, C ₆ H ₅) 7.09 (d, 2H, =CH-N), 6.34 (t, 2H = CH)	76%
	48-50°C	(MW:161.02) 161.05 99%	7.34 and 7.11 (2M, 4H, C ₆ H ₄) 7.01 (t, 2H, =CH-N), 6.34 (d, 2H, = CH)	70%
	Liquid	(MW: 179.02) 179.05 100%	6.65 ~ 6.9 (m, 3H, C ₆ H ₃) 7.02 (t, 2H, =CH-N), 6.34 (d, 2H, = CH)	73%

General procedure for preparation of pyrroles listed in Table VII:.

To a solution of 2.22g (20 mmol.) of p-fluoro-aniline in 20 ml of glacial acetic acid was added 3.17 g (24 mmol) of dimethoxytetrahydrofuran while stirring. After refluxing for 1 h, the solution was poured into 100 ml ice-water and extracted

with hexane (50 ml x3). The organic layer was separated and washed with brine and dried over anhyd MgSO₄. The solvent was removed under reduced pressure to give a crude solid. It was purified by flash column (silica gel using hexane as elute solvent to give white crystals, yield 2.24 g (70%)).

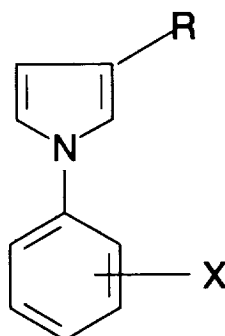
The acylation of the N-substituted pyrroles (Eq. 2) gave a mixture of 2- and 3-acylated N-substituted pyrroles. These two isomers could be separated by column chromatography.

It was found that SnCl₄ worked best as catalyst for this acylation.

The isolated 3-acylated pyrroles were attempted to be reduced. We found that neither LiAlH₄, NaAlH₂ (OCH₂CH₂OCH₃)₂, NaBH₄, Zn + HCl, nor B₂H₆ reduced the keto group (5,6). Finally we had success by transforming the keto group into a tosylhydrazone and reducing this hydrazone by B₂H₆ (7) (see Eq. 3).

The results are listed in Table II, below.

Table VIII



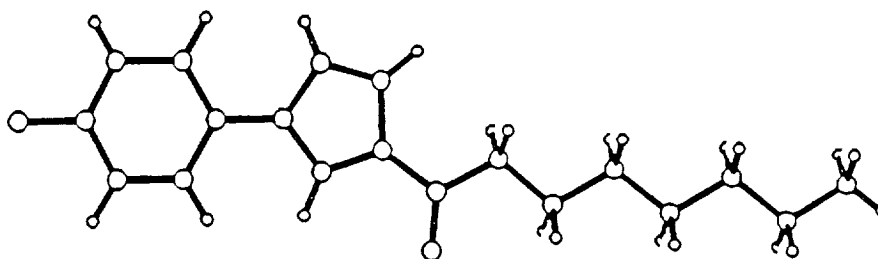
X	R=C ₈ H ₁₇	m.p.°C	C ₁₂ H ₂₈	m.p.°C	C ₁₆ H ₃₃	m.p.°C	C ₁₈ H ₃₇	m.p.°C
X=H	C _{calcd.} 84.65	28-30°	84.82	oil	84.95	60-62°C	84.99	oil
	C _{found} 84.67		84.65		84.89		84.87	
	H _{calcd.} 9.87		10.68		11.27		11.46	
	H _{found} 9.60		10.47		10.97		11.25	

X=4-F	C _{calcd.} 79.12	38-40°	80.24	49-51°	81.04	68-70°	81.35	60-62°
	C _{found} 78.96		80.29		80.95		81.27	
	H _{calcd.} 8.79		9.73		10.39		10.65	
	H _{found} 8.63		9.75		10.36		10.67	
X=3,5-F	C _{calcd.} 74.23	oil	--		--		77.95	46-48°
	C _{found} 74.36		--		--		78.09	
	H _{calcd.} 7.90		--		--		9.97	
	H _{found} 7.75		--		--		9.87	

All compounds were additionally characterized by ¹H-NMR, ¹³C-NMR and MS.

To be absolutely sure that our assignments of the 2- and 3-acylated pyrroles were correct, X-ray analysis of 1-(4-fluorophenyl)-3-octanoxylpyrrole was taken. As shown in Figure 1, our assignments agreed with the X-ray structure (Figure I and Tables IA, IB, and IC).

Figure I



BOND ANGLES (DEGREES) FOR C18H22FNO

N(1)-C(2)-H(2)	120.2(14)
H(2)-C(2)-C(3)	131.1(14)
C(3)-C(4)-H(4)	126.4(14)
H(4)-C(4)-C(5)	126.0(14)
N(1)-C(5)-H(5)	123.0(14)
C(4)-C(5)-H(5)	127.9(14)
C(1')-C(2')-H(2')	118.5(13)
H(2')-C(2')-C(3')	121.4(13)
C(2')-C(3')-H(3')	121.8(16)
H(3')-C(3')-C(4')	119.3(16)
C(4')-C(5')-H(5')	122.1(16)
H(5')-C(5')-C(6')	119.4(16)
C(1')-C(6')-H(6')	119.8(15)
C(5')-C(6')-H(6')	119.6(15)
C(1'')-C(2'')-H(2a'')	107.7(14)
C(1'')-C(2'')-H(2b'')	107.8(13)
H(2a'')-C(2'')-H(2b'')	107.6(20)
H(2a'')-C(2'')-C(3'')	108.9(14)
H(2b'')-C(2'')-C(3'')	109.9(16)
C(2'')-C(3'')-H(3a'')	110.0(11)
C(2'')-C(3'')-H(3b'')	109.5(13)
H(3a'')-C(3'')-H(3b'')	103.5(17)
H(3a'')-C(3'')-C(4'')	109.9(12)
H(3b'')-C(3'')-C(4'')	110.9(11)
C(3'')-C(4'')-H(4a'')	109.1(12)
C(3'')-C(4'')-H(4b'')	109.4(11)
H(4a'')-C(4'')-H(4b'')	104.8(17)
H(4a'')-C(4'')-C(5'')	109.2(11)
H(4b'')-C(4'')-C(5'')	109.8(14)
C(4'')-C(5'')-H(5a'')	109.5(13)
C(4'')-C(5'')-H(5b'')	109.0(14)
H(5a'')-C(5'')-H(5b'')	104.5(20)
H(5a'')-C(5'')-C(6'')	110.9(14)
H(5b'')-C(5'')-C(6'')	109.3(12)
C(5'')-C(6'')-H(6a'')	107.4(13)
C(5'')-C(6'')-H(6b'')	108.6(10)
H(6a'')-C(6'')-H(6b'')	107.2(17)
H(6a'')-C(6'')-C(7'')	110.8(12)
H(6b'')-C(6'')-C(7'')	108.6(13)
C(6'')-C(7'')-H(7a'')	109.0(15)
C(6'')-C(7'')-H(7b'')	107.1(15)
H(7a'')-C(7'')-H(7b'')	108.9(22)
H(7a'')-C(7'')-C(8'')	109.3(16)
H(7b'')-C(7'')-C(8'')	109.4(13)
C(7'')-C(8'')-H(8a'')	113.9(16)
C(7'')-C(8'')-H(8b'')	108.8(18)
H(8a'')-C(8'')-H(8b'')	109.6(30)
C(7'')-C(8'')-H(8c'')	108.1(22)
H(8a'')-C(8'')-H(8c'')	111.2(28)
H(8b'')-C(8'')-H(8c'')	104.9(30)

Table IB

BOND ANGLES (DEGREES) FOR C18H22FNO

C(2)-N(1)-C(5)	107.9(2)
C(2)-N(1)-C(1')	126.7(2)
C(5)-N(1)-C(1')	125.4(2)
N(1)-C(2)-C(3)	108.7(2)
C(2)-C(3)-C(4)	106.8(2)
C(2)-C(3)-C(1'')	124.9(2)
C(4)-C(3)-C(1'')	128.2(2)
C(3)-C(4)-C(5)	107.6(2)
N(1)-C(5)-C(4)	109.0(2)
N(1)-C(1')-C(2')	120.5(2)
N(1)-C(1')-C(6')	120.3(2)
C(2')-C(1')-C(6')	119.3(2)
C(1')-C(2')-C(3')	120.1(2)
C(2')-C(3')-C(4')	118.9(2)
F'-C(4')-C(3')	118.6(2)
F'-C(4')-C(5')	118.8(2)
C(3')-C(4')-C(5')	122.6(2)
C(4')-C(5')-C(6')	118.4(2)
C(1')-C(6')-C(5')	120.6(2)
C(3)-C(1'')-O''	121.2(2)
C(3)-C(1'')-C(2'')	117.6(2)
O''-C(1'')-C(2'')	121.2(2)
C(1'')-C(2'')-C(3'')	114.6(2)
C(2'')-C(3'')-C(4'')	112.7(2)
C(3'')-C(4'')-C(5'')	114.1(2)
C(4'')-C(5'')-C(6'')	113.3(2)
C(5'')-C(6'')-C(7'')	114.0(2)
C(6'')-C(7'')-C(8'')	113.0(2)

Table IC

BOND DISTANCES (ANGSTROMS) FOR C18H22FNO

N(1)-C(2)	1.371	(3)
N(1)-C(5)	1.382	(3)
N(1)-C(1')	1.428	(3)
C(2)-C(3)	1.370	(3)
C(3)-C(4)	1.422	(3)
C(3)-C(1'')	1.469	(3)
C(4)-C(5)	1.347	(3)
F'-C(4')	1.364	(3)
C(1')-C(2')	1.388	(3)
C(1')-C(6')	1.383	(3)
C(2')-C(3')	1.377	(3)
C(3')-C(4')	1.368	(4)
C(4')-C(5')	1.359	(3)
C(5')-C(6')	1.384	(3)
O''-C(1'')	1.223	(3)
C(1'')-C(2'')	1.499	(3)
C(2'')-C(3'')	1.517	(3)
C(3'')-C(4'')	1.519	(3)
C(4'')-C(5'')	1.522	(3)
C(5'')-C(6'')	1.514	(3)
C(6'')-C(7'')	1.521	(3)
C(7'')-C(8'')	1.513	(4)
C(2)-H(2)	0.968	(22)
C(4)-H(4)	0.981	(21)
C(5)-H(5)	0.905	(25)
C(2')-H(2')	0.950	(25)
C(3')-H(3')	0.977	(26)
C(5')-H(5')	0.912	(29)
C(6')-H(6')	1.011	(25)
C(2'')-H(2a'')	0.974	(26)
C(2'')-H(2b'')	0.986	(26)
C(3'')-H(3a'')	1.002	(23)
C(3'')-H(3b'')	1.005	(23)
C(4'')-H(4a'')	1.015	(23)
C(4'')-H(4b'')	0.990	(23)
C(5'')-H(5a'')	0.961	(27)
C(5'')-H(5b'')	1.021	(25)
C(6'')-H(6a'')	1.021	(25)
C(6'')-H(6b'')	0.997	(22)
C(7'')-H(7a'')	0.998	(31)
C(7'')-H(7b'')	1.020	(27)
C(8'')-H(8a'')	0.963	(33)
C(8'')-H(8b'')	0.980	(38)
C(8'')-H(8c'')	1.001	(41)

General Procedures for the Reduction of the 3-Acyl-1-Arypyrroles. (3-Palmitoyl)-1-(4'-fluorophenyl)-pyrrole. A 500 ml round bottom flask equipped with a reflux condenser was charged with 2.2 g (5.5 mmol) of 3-palmitoyl-1-(4'-fluorophenyl)pyrrole in 50 ml dry THF. To this, 1.54g (8.25 mmol 1.5 eq) of tosylhydrazide was added, the mixture was heated under gentle reflux for 12 hours, then cooled to room temperature. To the solution was added 60 ml 3M diborane in THF, (excess amount) while stirring for 5 hours at room temperature. It was then refluxed overnight. The solution was quenched with methanol, the solvent removed by evaporation, and the residue extracted with ethyl acetate. The organic layer was washed and dried, removing solvent to give a crude product. Flash column purification by using hexane as the elute solvent gave 0.98 g white crystals (1 m.p., 46-48°C) with a yield of 46.2%.

Electrochemical Polymerization Studies:

As model compounds 1-phenylpyrrole and 1-(4-fluorophenyl)-pyrrole were chosen for testing their suitability for film production by electrochemical polymerization on a Pt-electrode and a Ga-As electrode.

Results:

1-Phenylpyrrole and 1-(4-fluoro)phenylpyrrole (5 mmol each) were dissolved in 12 ml of 0.5 M NaClO₄acetonitrile. While 1-phenylpyrrole did not show any indication of film formation on either of the electrodes, the 1-(4-fluorophenyl)pyrrole deposited a very thin black film on the Pt-electrode. The 1-phenyl derivative did not form a film. Both materials did not deposit a film on the GaAs wafer.

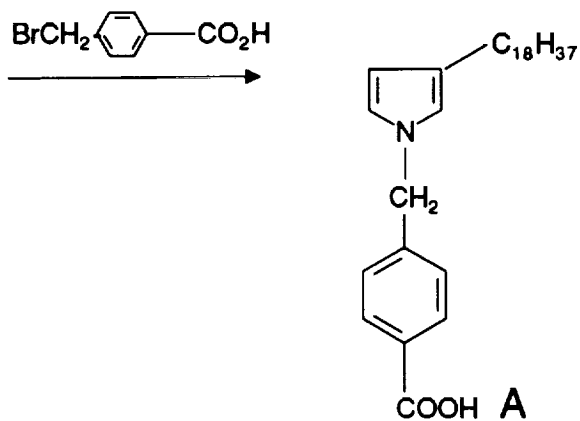
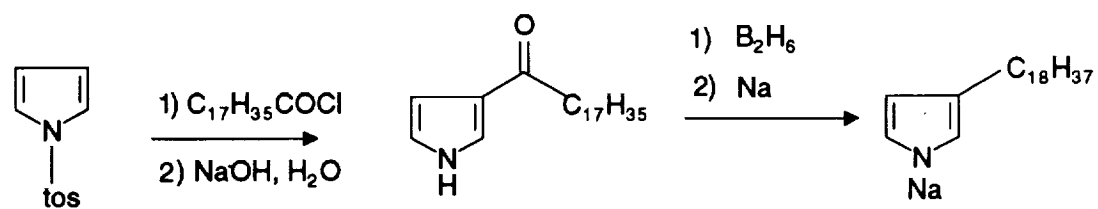
N-Benzyl-3-Long-Chain Substituted Pyrroles

To enhance the hydrophilic character of the monomers and thus increase their ability to form Langmuir-Blodgett films, the structure of the pyrrole-based monomers were altered somewhat. It was thought that 1-benzylsubstituted pyrroles might be better for Langmuir-Blodgett film formation. As a target compound we chose to synthesize 1-(4-carboxyphenyl)-methyl-3-stearylpyrrole A.

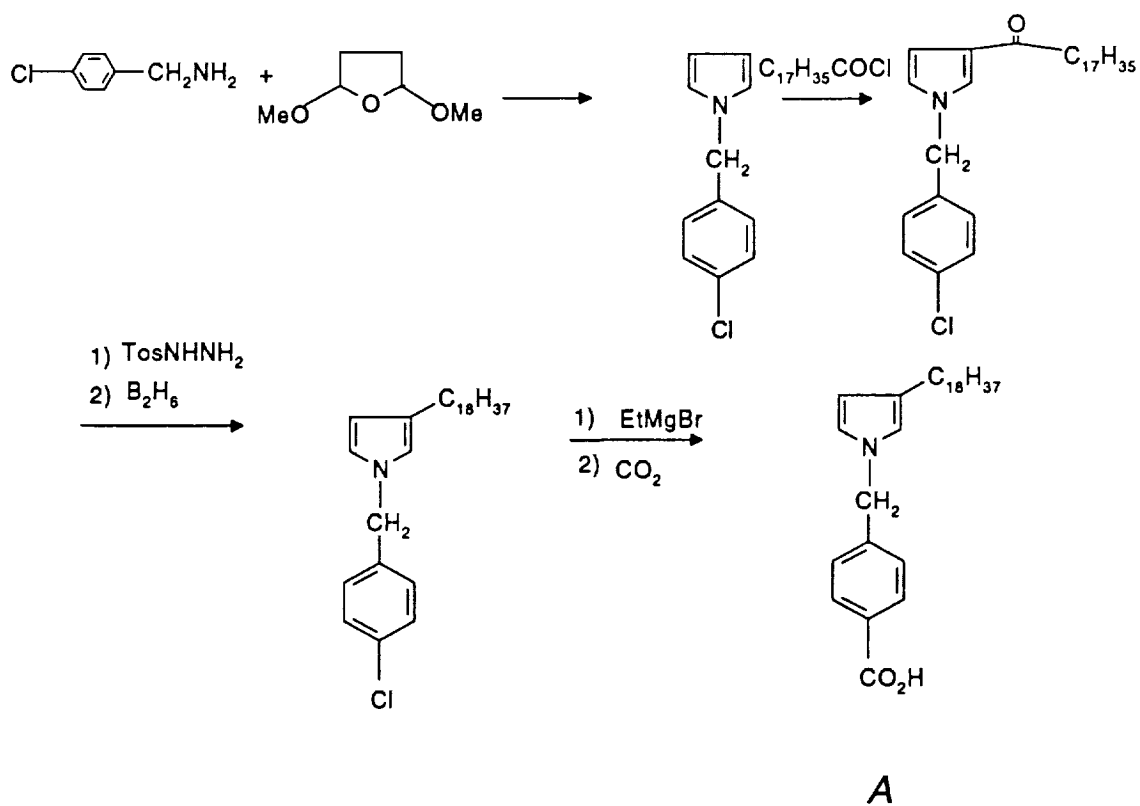
The synthesis of A proved to be more difficult, as anticipated.

The unsuccessful routes will only be outlined briefly.

Starting material was the known N-tosylpyrrole. The following sequence should give A:

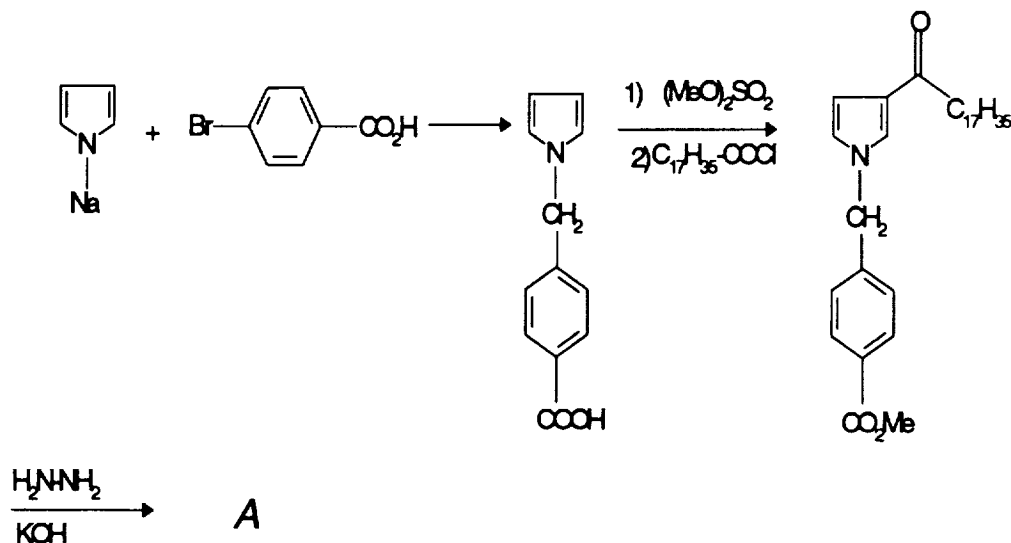


However, the last step could not be made to work. Therefore, this route was abandoned and the following sequence was tried.



However, again the last step, the conversion of the 4-chloroderivative into the corresponding Grignard compound could not be achieved.

Finally, we obtained the desired A by the following sequence:



The successful synthesis proceeded as follows:

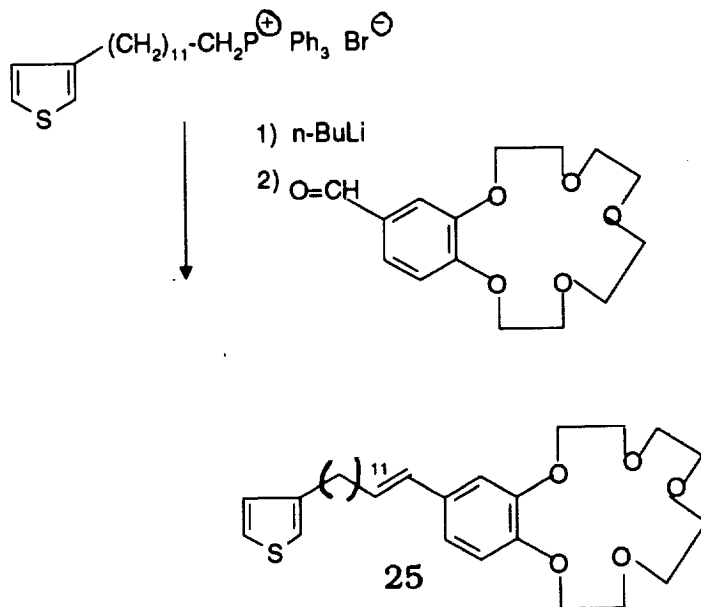
1-(4-Carboxylphenylmethyl)pyrrole, 1. To a dispersion of NaH (0.96g, 20 nmol) a DMF-solution of pyrrole was added dropwise (N_2) when immediately a vigorous H_2 -generation was observed. After stirring for 2 hrs. 2.15 g (10 nmol) of 4-bromomethylbenzoic acid was added. After stirring overnight the reaction mixture was quenched with 1N aqueous HCl and extracted with ethyl acetate (100 ml x 3). The organic layer was dried with anhydrous MgSO_6 ; the solvent was distilled off to leave a solid which after flash column purification gave 1 as colorless crystals (1.1g, 55% yield). $^1\text{H NMR}$ (CDCl_3) 5.14 (s, 2H, CH_2), 6.22 (d, 2H, $J=2.5$ Hz); 6.69 (d, 2H, $J=2.5$ Hz); 7.16 (d, 2H $J=7.5$ Hz); 8.06 (d, 2H, $J=7.5$ Hz). MS 201 (M^+ , 14).

1-Methyl ester, 2; to acid 1 (1.52 g, 7.56 mmol) dissolved in 100 ml anhydrous acetone in a 500 ml flask was added dimethyl sulfate (1.14 g, 9.07 mmol) and K_2CO_3 (1.26 g, 9.07 mmol). This mixture was refluxed for 5 h. The formed solid was removed by filtration and the solvent was distilled to give crude 2 1.6 g (quantitative yield). It was directly used in the next step without purification. $^1\text{H NMR}$ (CDCl_3) 3.88 (s, 3H, CH_3); 5.10 (s, 2H, CH_2); 6.20 (d, 2H, $J=2$ Hz); 6.67 (d, 2H, $J=2$ Hz); 7.11 (d, 2H, $J=7.5$ Hz); 7.96 (d, 2H, $J=7.5$ Hz).

Methyl-1-(4-carboxylbenzyl)-3-stearylpyrrole **3**. To a solution of **2** 1.64 g, (7.6 mmol) in benzene a suspension of 1.5 g (8.5 mmol) stannous chloride and 3.4 g (8.5 mmol) stearyl chloride was added slowly while stirring at 0° for 1 hr and an additional hr at room temperature. Quenching with aqueous 1N HCl gave after flask column purification 1.95 g of crude **3** and .54 g of the 2-isomer for a combined yield of 67.9%. ¹H NMR (CDCl₃) 0.87 (t, 3H, J=7 Hz); 1.25 (m, 28H); 1.60 (m, 2H); 2.72 (t, 2H, J=7.5 Hz); 3.88 (s, 3H); 5.63 (s, 2H); 6.22 (m, 1H); 6.92 (m, 1H); 7.03 (m, 1H); 7.09 (d, 2H, J=7.5 Hz); 7.95 (d, 2H, J=7.5 Hz); MS 481 (M⁺, 890).

1-(4-Carboxylbenzyl)-3-stearylpyrrole **4**; the ketone **3** was dissolved in 100 ml diethylene glycol when .58 g (10.4 mmol) KOH and .83 g (10.4 mmol) was added. This solution was refluxed until the temperature reached 210°C. The mixture was quenched with 1N HCl. It was extracted with EtOAc (75 ml x 3) and the organic layer was separated, washed and dried. After removal of solvent it gave a solid product; flash column purification yielded 0.53 colorless crystal of **4** (56.4%). ¹H NMR (CDCl₃) 0.87 (t, 3H, J=7.5 Hz); 1.24 (m, 30H); 1.54 (m, 2H); 2.39 (t, 2H, J=7.5 Hz); 5.11 (s, 2H); 5.98 (m, 1H); 6.16 (m, 1H); 6.62 (m, 1H); 7.04 (d, 2H, J=7.5 Hz); 8.04 (d, 2H, J=7.5 Hz); 10.87 (s, 1H). ¹³C NMR 14.1, 22.66, 26.12, 28.73, 29.37, 29.54, 29.67, 31.89, 49.93, 106.17, 107.47, 120.71, 126.15, 128.42, 130.62, 133.63, 144.87, 171.85. MS 453 (M⁺, 17) IR (CM, CHCl₃) 3019.2, 2925.1, 2851.4, 2400.3, 1692.7, 1612.5, 1578.2, 1512.5, 1484.5, 1469.9, 1422.4, 1280.2, 1215.4, 1125, 1076, 1018.8. MP 97-99°C.

Finally a compound in which a 15-benzocrown[6]-ether aldehyde is attached via an alkylidene chain to a thiophene was synthesized. It was obtained by the following route:

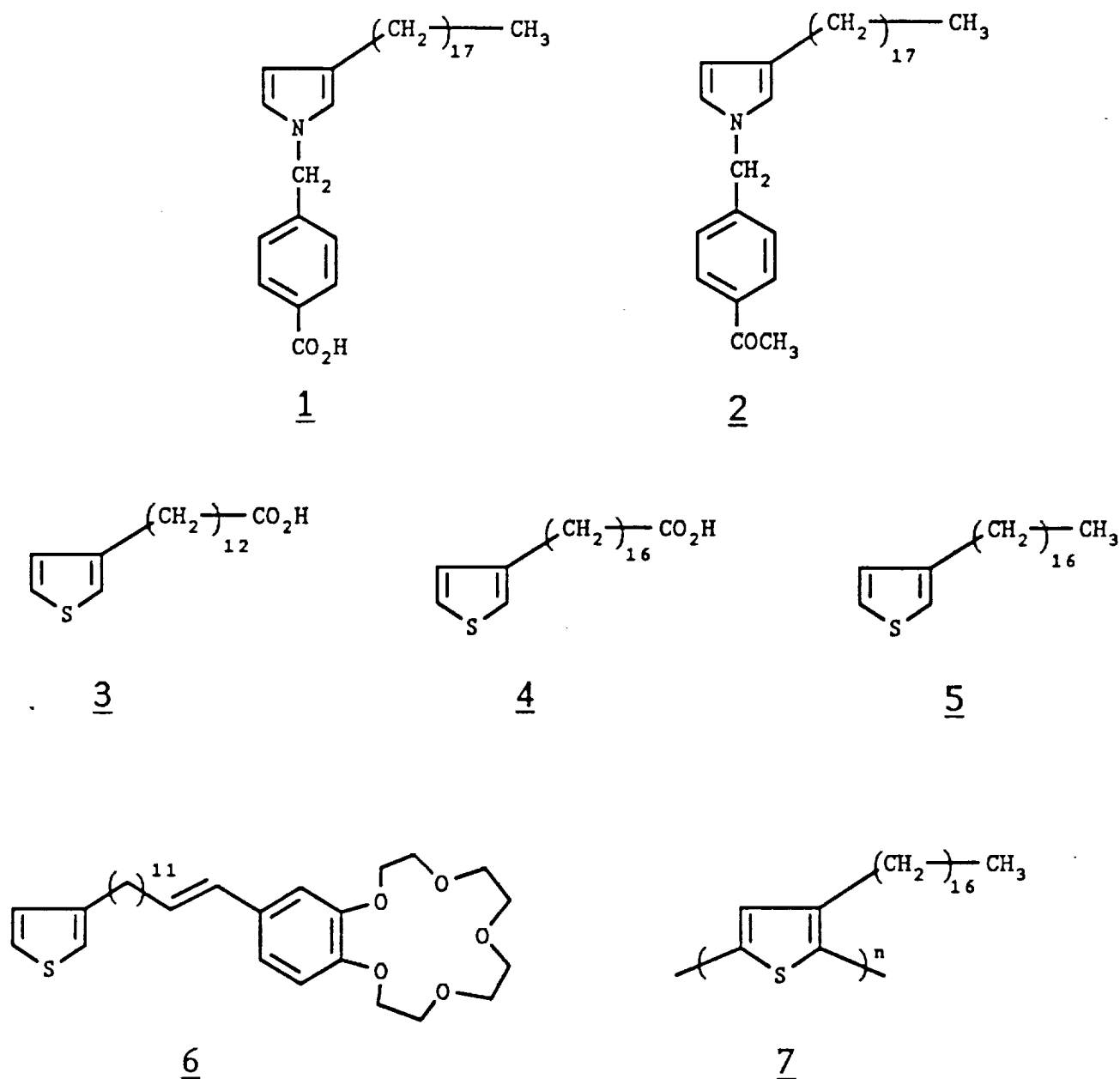


It was identified by $^1\text{H-NMR}$.

Results of Test for Langmuir-Blodgett Film Formation

A total of seven compounds were tested for Langmuir-Blodgett film formation. They are shown in Figure 2

Figure 2:



Results:

All experiments involving langmuir-Blodgett film formation were done at the laboratories of Professor J. Lando at Case Western Reserve University in Cleveland, Ohio. The work was done under Professor Lando's supervision by Ms. Cynthia Striley.

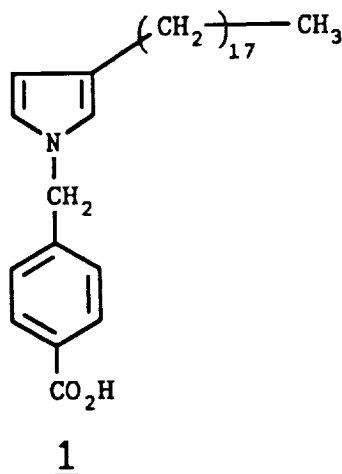
Surface Pressure vs. Molecular Area Isotherms:

Description of Experiments:

The compounds shown in Figure 2 were analyzed for their ability to form Langmuir-Blodgett films. Most tests were run in duplicate and each material was tested on pure water and a cadmium subphase (CdCl_2 , pH 5). The resulting surface pressure vs. molecular isotherm plots are shown after characterization of the materials of interest. It became obvious that compounds 1,7 and perhaps 4 were forming Langmuir-Blodgett films on a cadmium subphase. The results of all the tests performed will be briefly discussed.

Results of Isotherm Experiments:

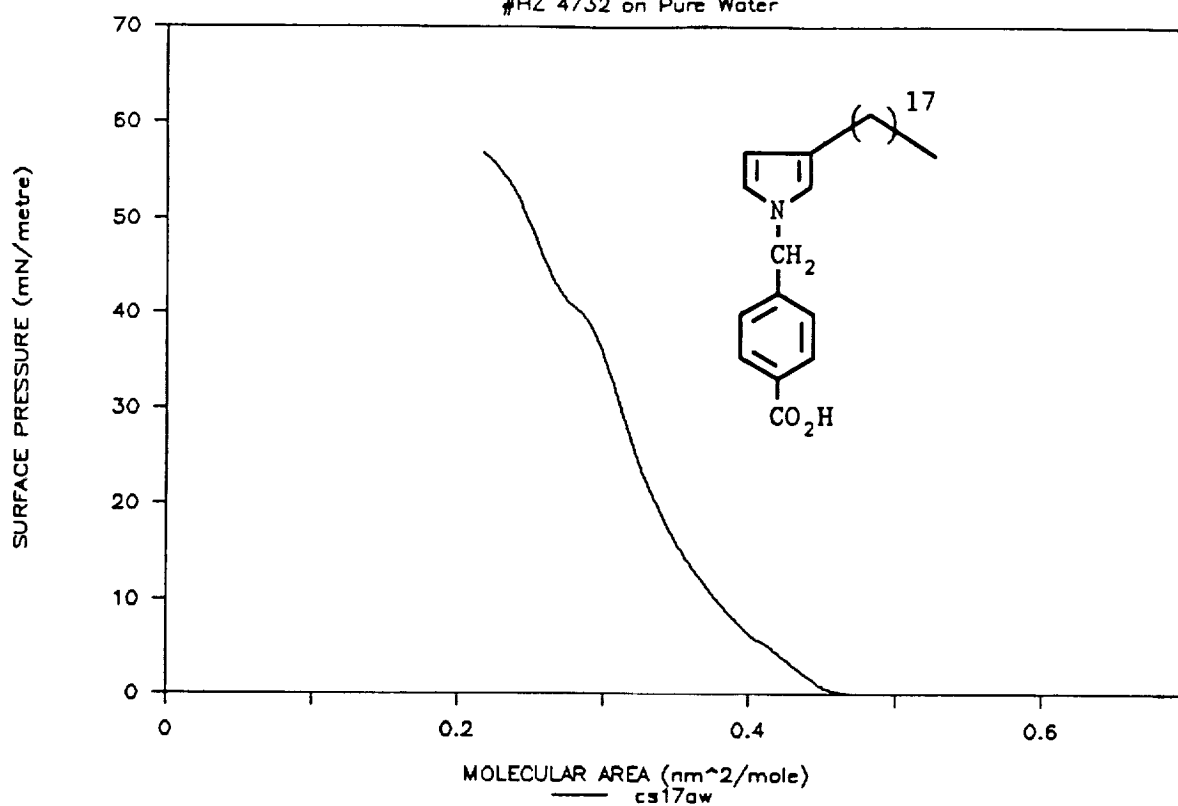
Compound 1



Compound 1 was first tested on a subphase of pure water. The resulting isotherm looked promising in that the surface pressure reached a good level over molecular area range that signifies the formation of a monolayer. Compound 1 was then run upon a subphase of cadmium chloride at pH = 5. The effect of the cadmium ion and the pH with the carboxyl functionality seemed to stabilize the hydrophilic portion of the molecule with the subphase. The steeper slope of the isotherm may be interpreted as the formation of a film upon the surface, but since the inflection point of the isotherm is not centered over a molecular area of 0.2 nm²/mole, a close packed monolayer has not been achieved. Still, this result is very promising, and deposition studies should be performed.

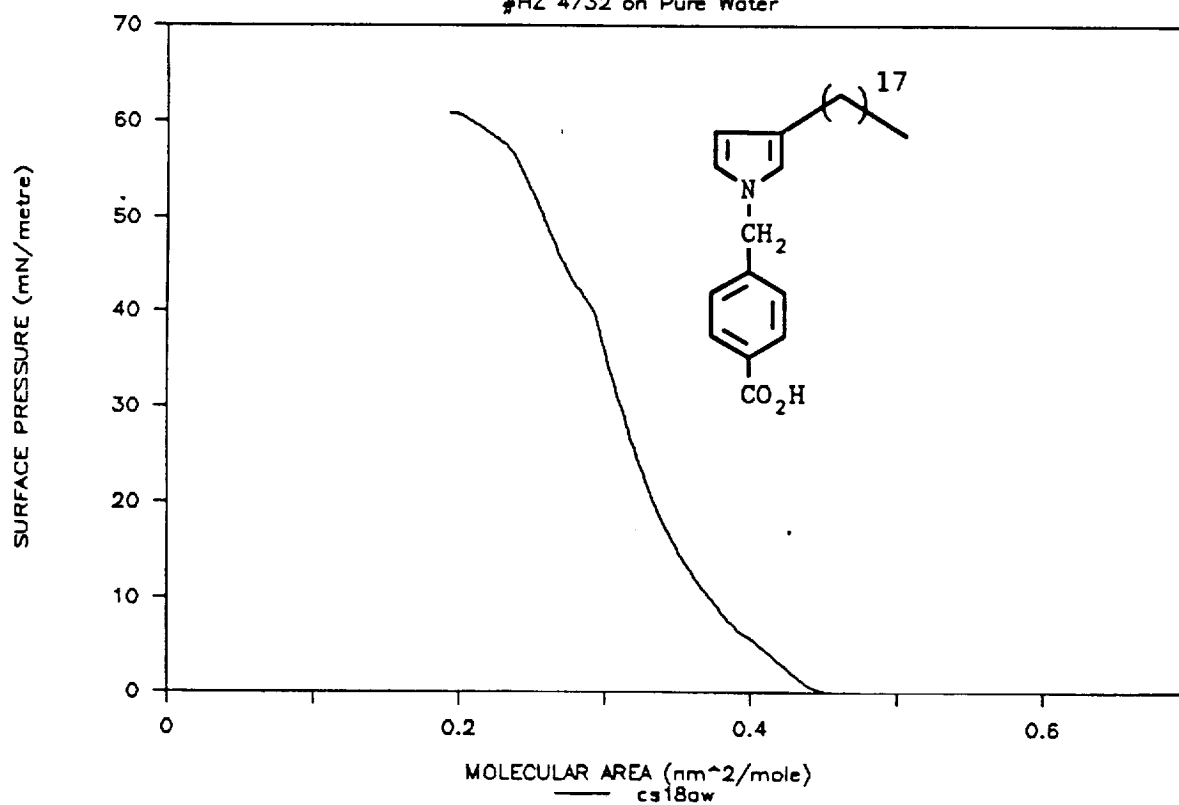
SURFACE PRESSURE vs. MOLECULAR AREA

#HZ 4732 on Pure Water



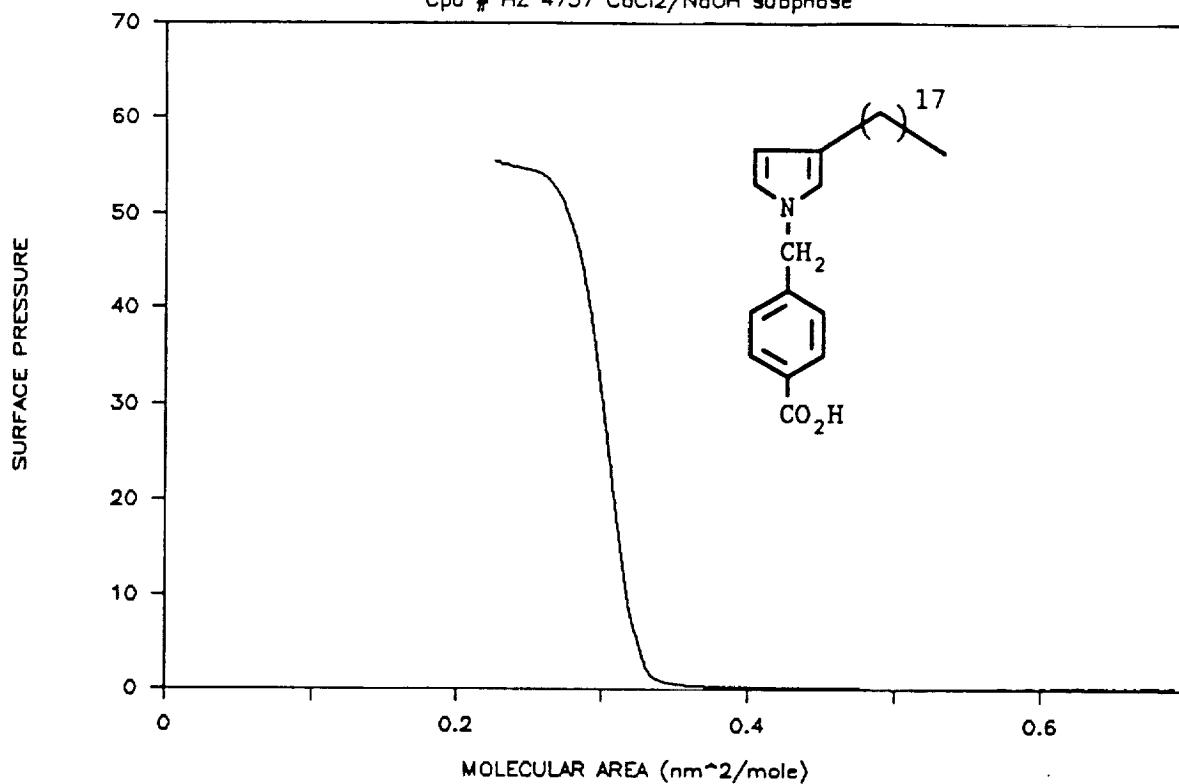
SURFACE PRESSURE vs. MOLECULAR AREA

#HZ 4732 on Pure Water



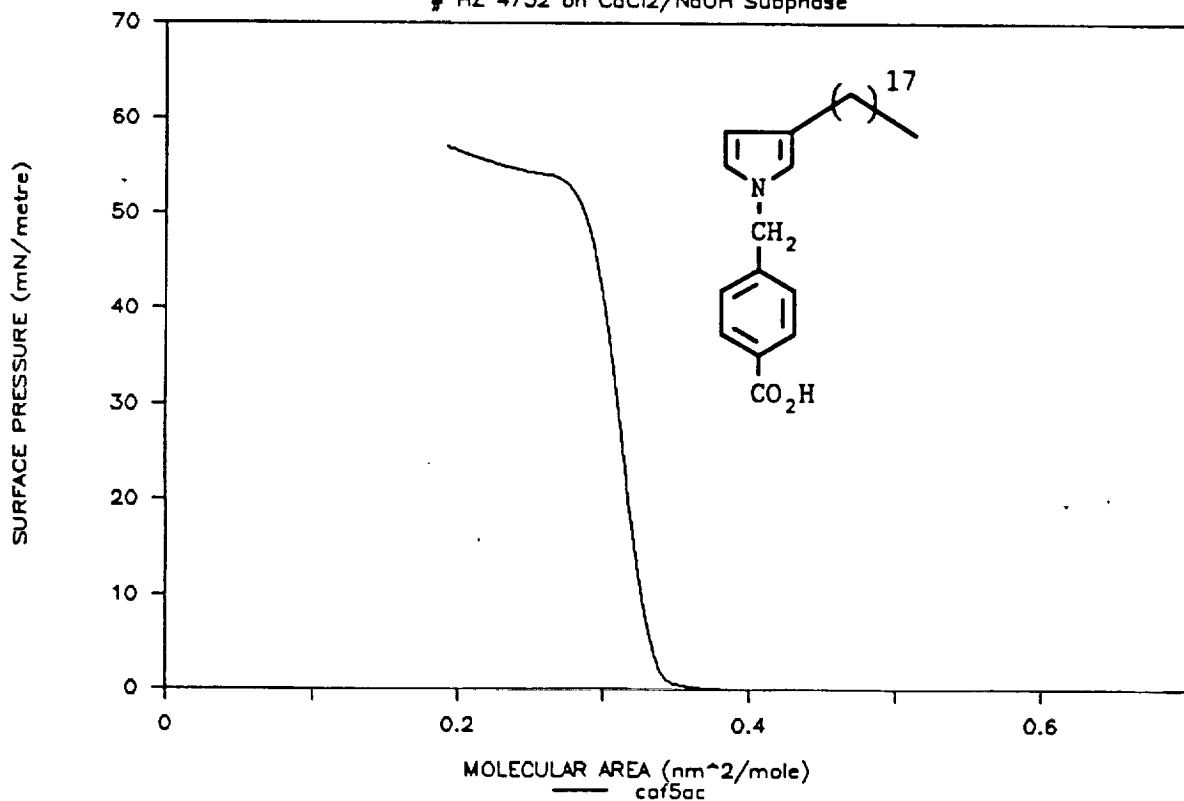
SURFACE PRESSURE vs. MOLECULAR AREA

Cpd # HZ 4737 CdCl₂/NaOH subphase

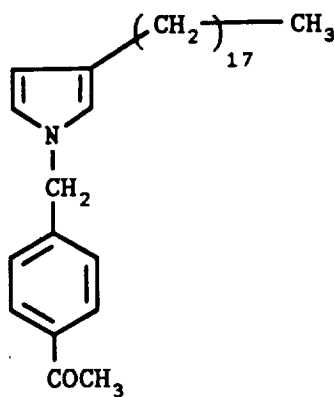


SURFACE PRESSURE vs. MOLECULAR AREA

HZ 4732 on CdCl₂/NaOH Subphase



Compound 2

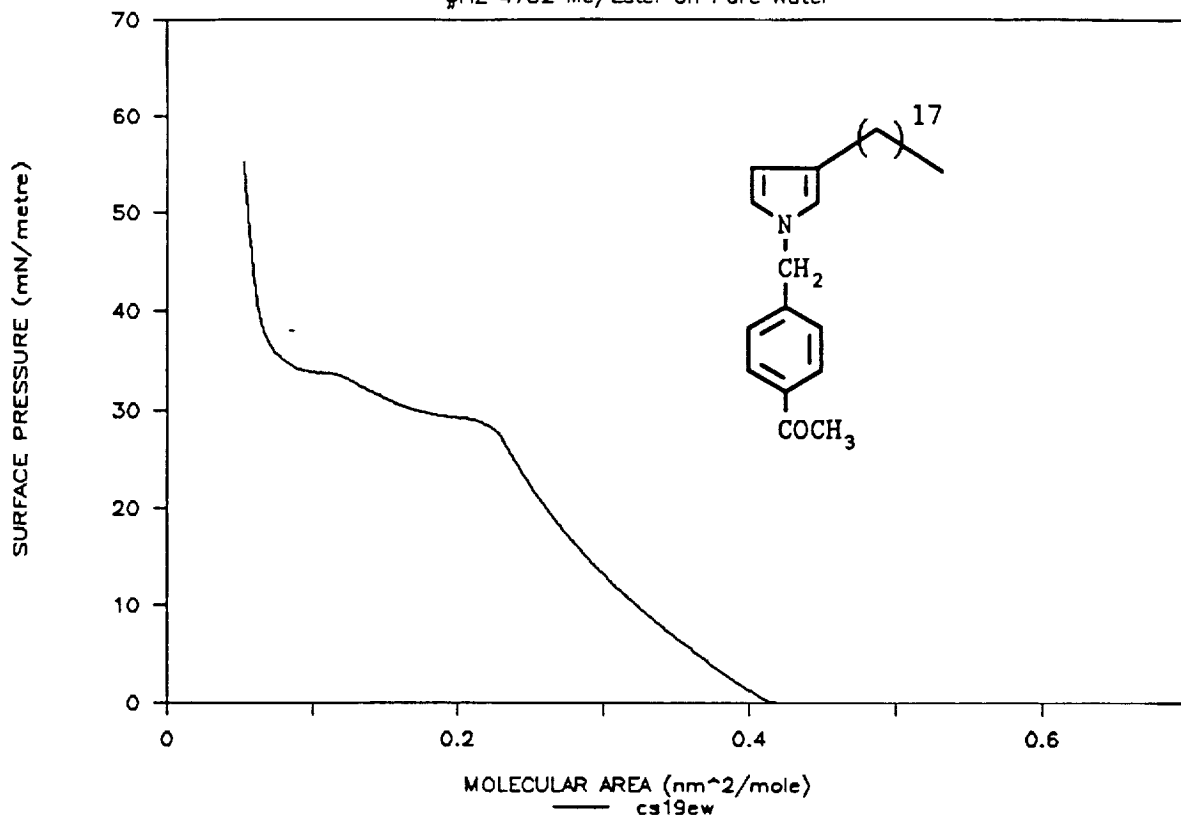


2

Compound 2 is the methyl ester of Compound 1. It was tested to see how much of the film forming ability could be attributed to the carboxyl functionality. The compound was tested upon subphases of pure water and cadmium chloride at pH = 5. The subphase has little effect on the improvement of the isotherm. This data shows that no film or monolayer is formed, and that the carboxyl group is key in the formation of a stable langmuir-Blodgett film.

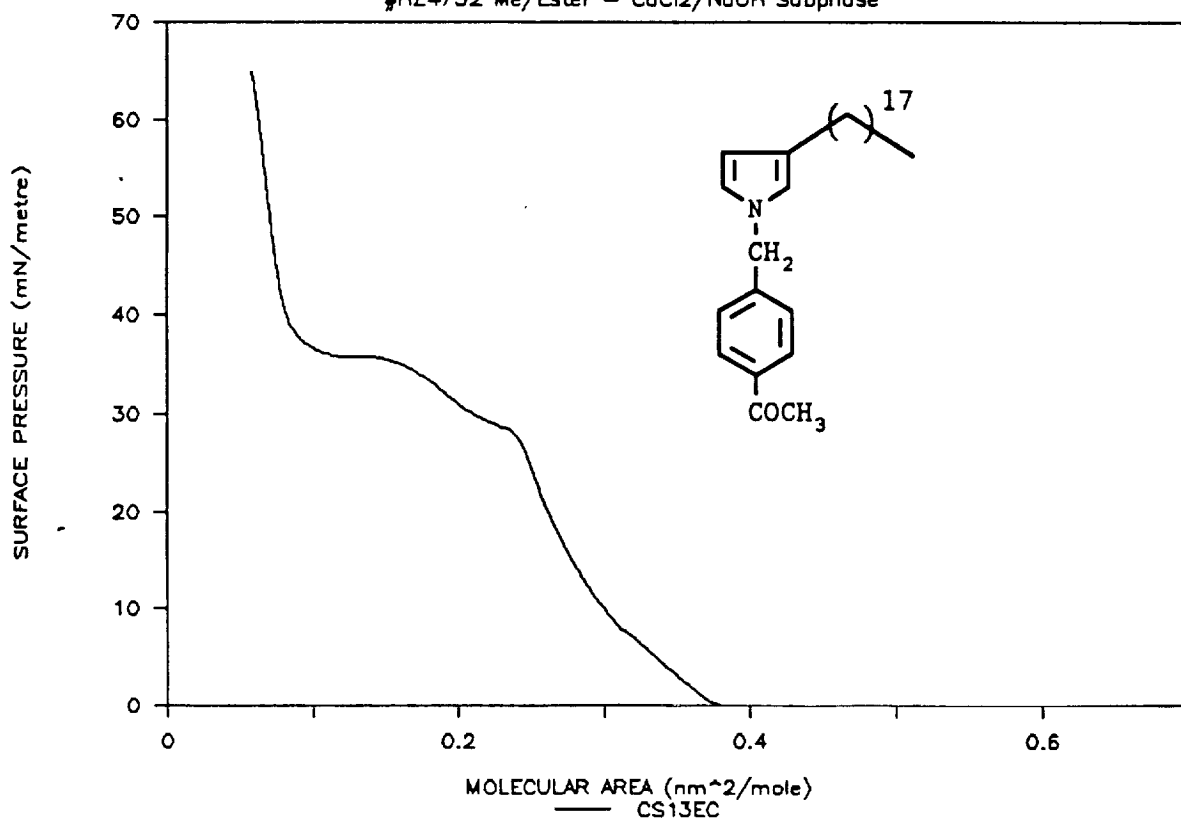
SURFACE PRESSURE vs MOLECULAR AREA

#HZ 4732 Me/Ester on Pure Water

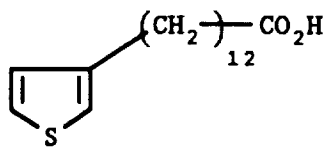


SURFACE PRESSURE vs. MOLECULAR AREA

#HZ4732 Me/Ester - CdCl₂/NaOH Subphase



Compound 3



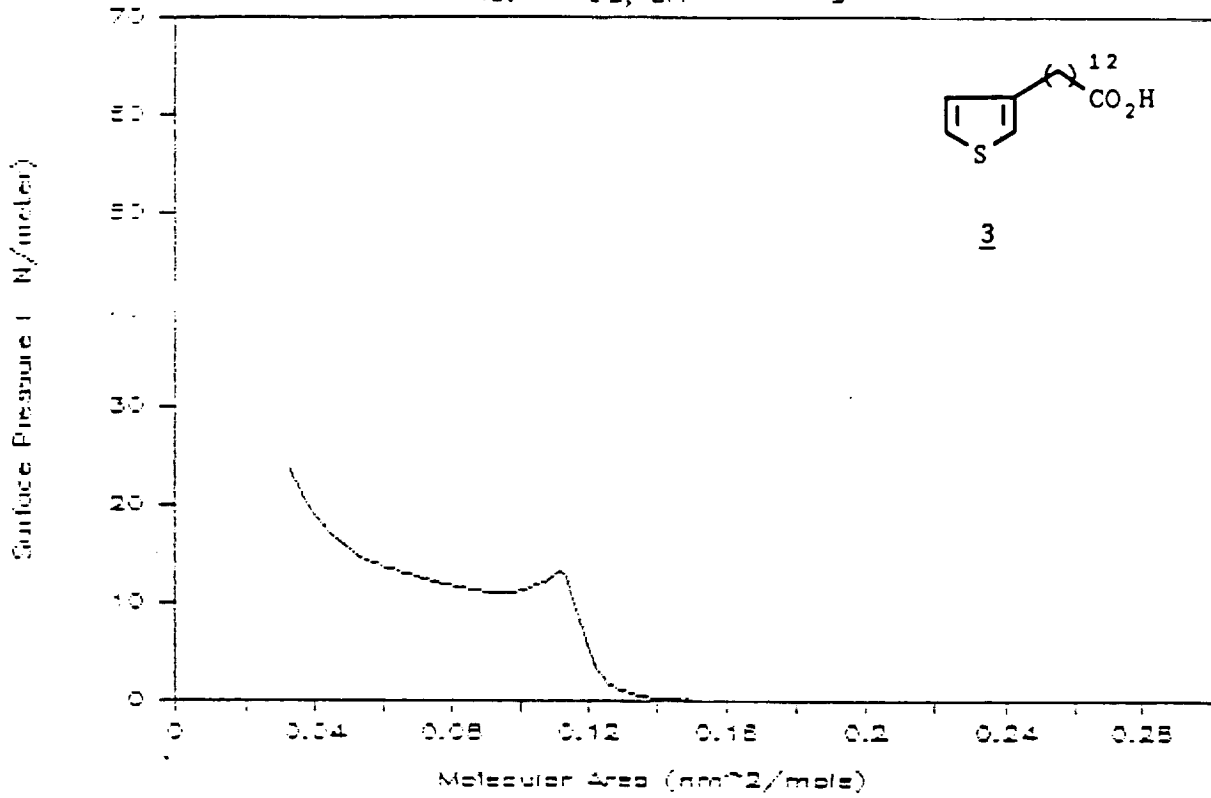
3

The isotherm for compound 3 reaches surface pressures far below the expected values for monolayer formation. The material is behaving "liquid-like". This result may be due to the relatively short C12 chain.

Isotherm of ≈ 4745 Hz on CdCl₂ Subphase

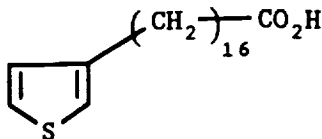
file: 47703, pH

3



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OF POOR QUALITY

Compound 4

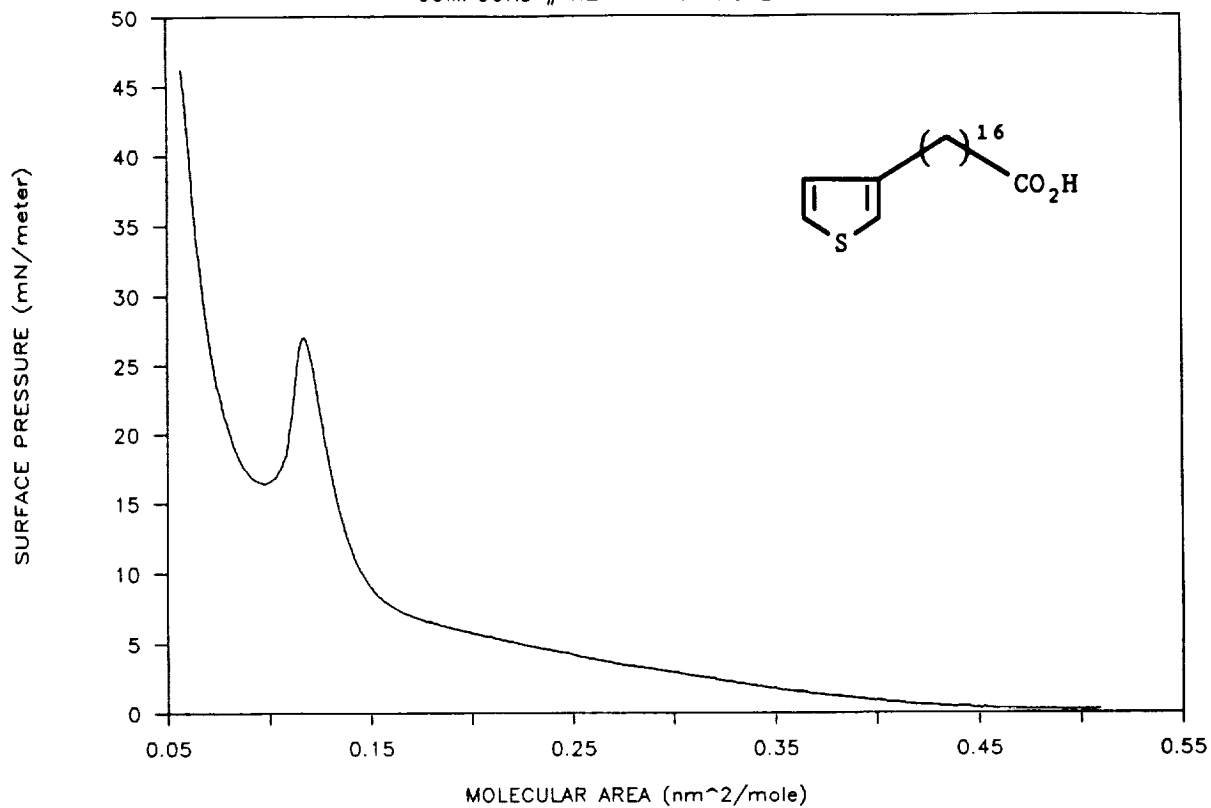


4

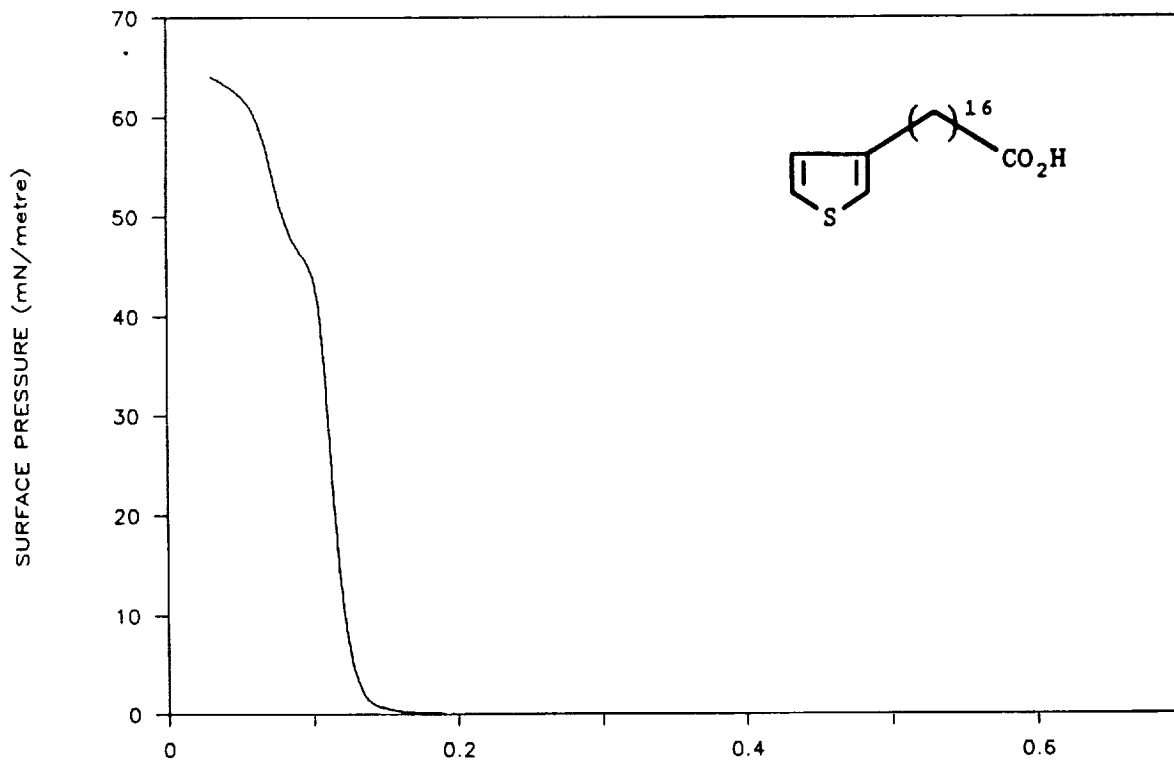
The isotherm of compound 4 on a pure water subphase is uncommon. Although it does not have the characteristics of a close packed monolayer, it suggests some type of ordered surface structure. When the subphase is changed to cadmium chloride the isotherm is altered, but the molecular area is so low that multiple layers are predicted. Those multiple layers may not have an ordered structure.

SURFACE PRESSURE vs. MOLECULAR AREA

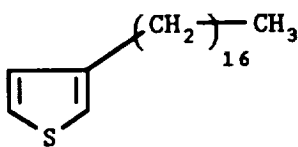
COMPOUND # HZ 4746 ON PURE WATER



SURFACE PRESSURE vs. MOLECULAR AREA



Compound 5

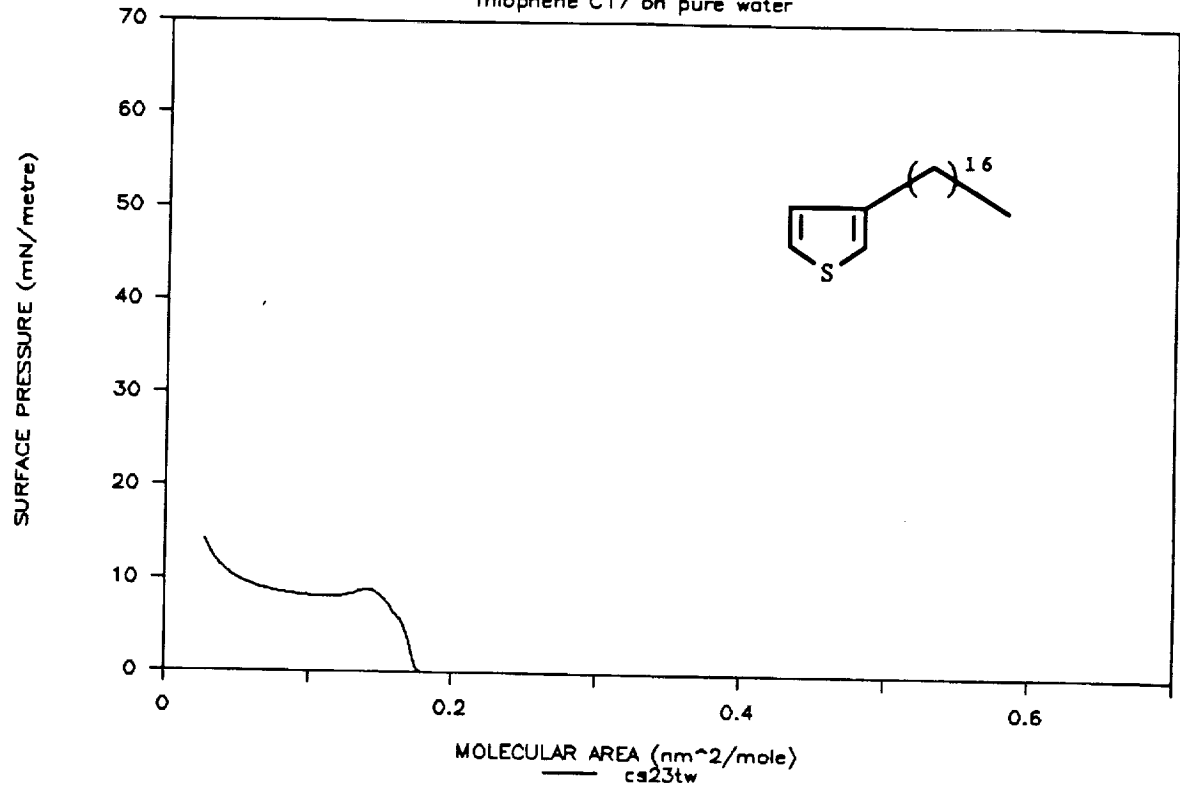


5

Compound 5 gave surface pressure values too low for monolayer formation. Choice of subphase makes little difference in the maximum pressure achieved. This material behaves like a liquid on the surface.

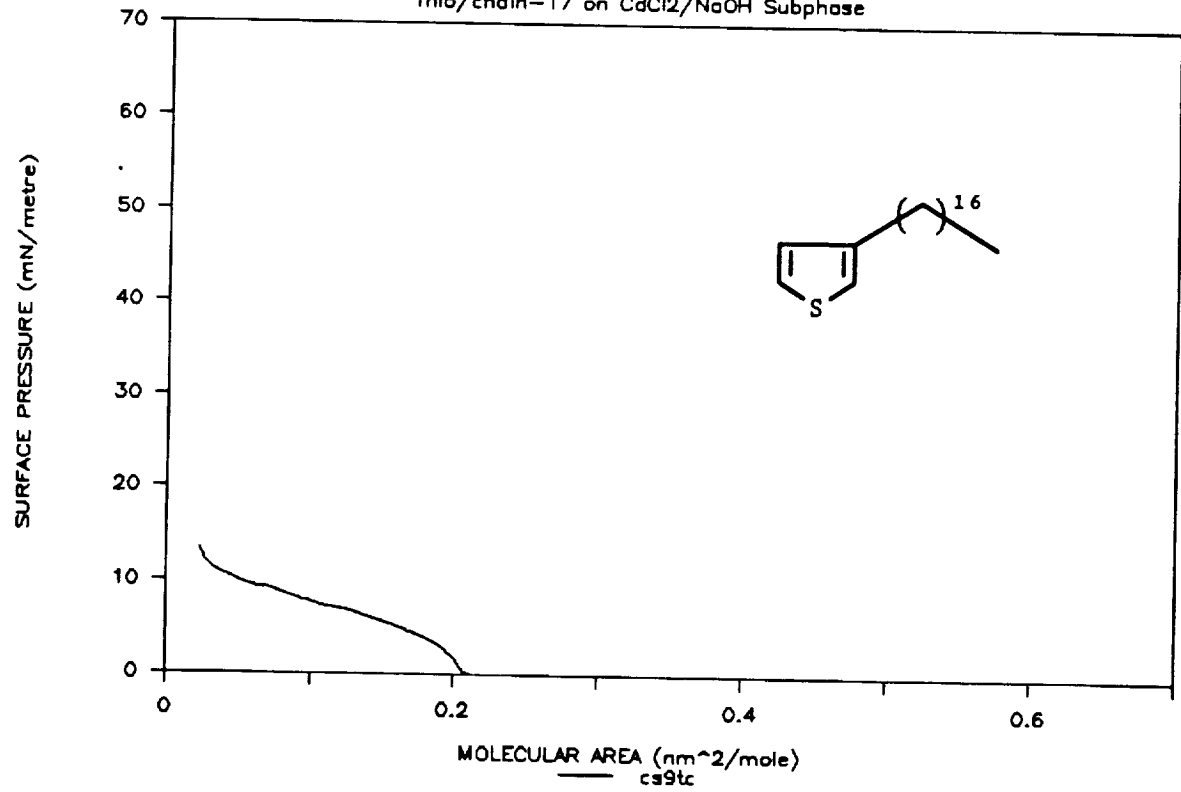
SURFACE PRESSURE vs. MOLECULAR AREA

Thiophene C17 on pure water

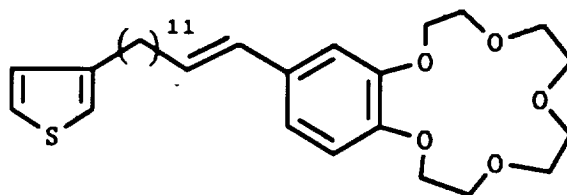


SURFACE PRESSURE vs. MOLECULAR AREA

Thio/chain-17 on CdCl₂/NaOH Subphase



Compound 6

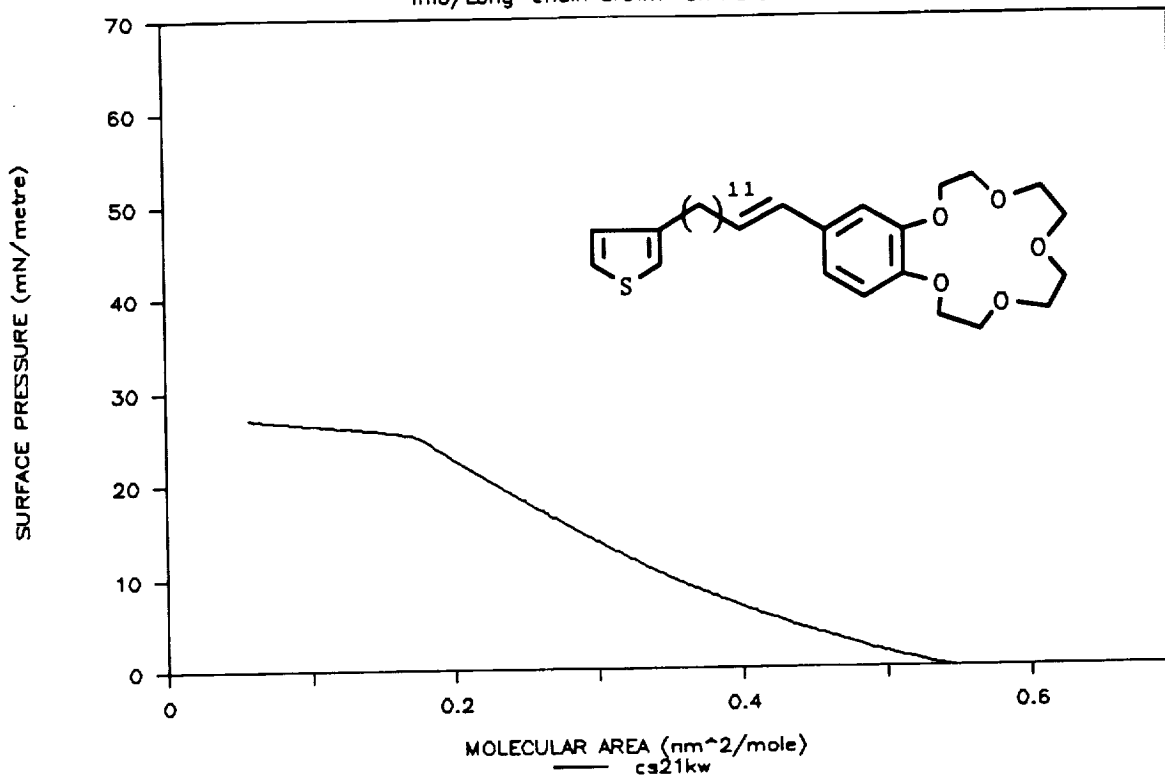


6

Compound 6 does not form a monolayer or any film at all upon either a pure water subphase or a cadmium chloride subphase. Due to the limit of time extra tests were not performed. It would be useful to modify the subphase to accommodate the crown ether's cavity size. If an interaction with the subphase can be established, perhaps film formation may occur. The conclusion of this data suggests that cadmium ion does not interact appreciably with the crown cavity.

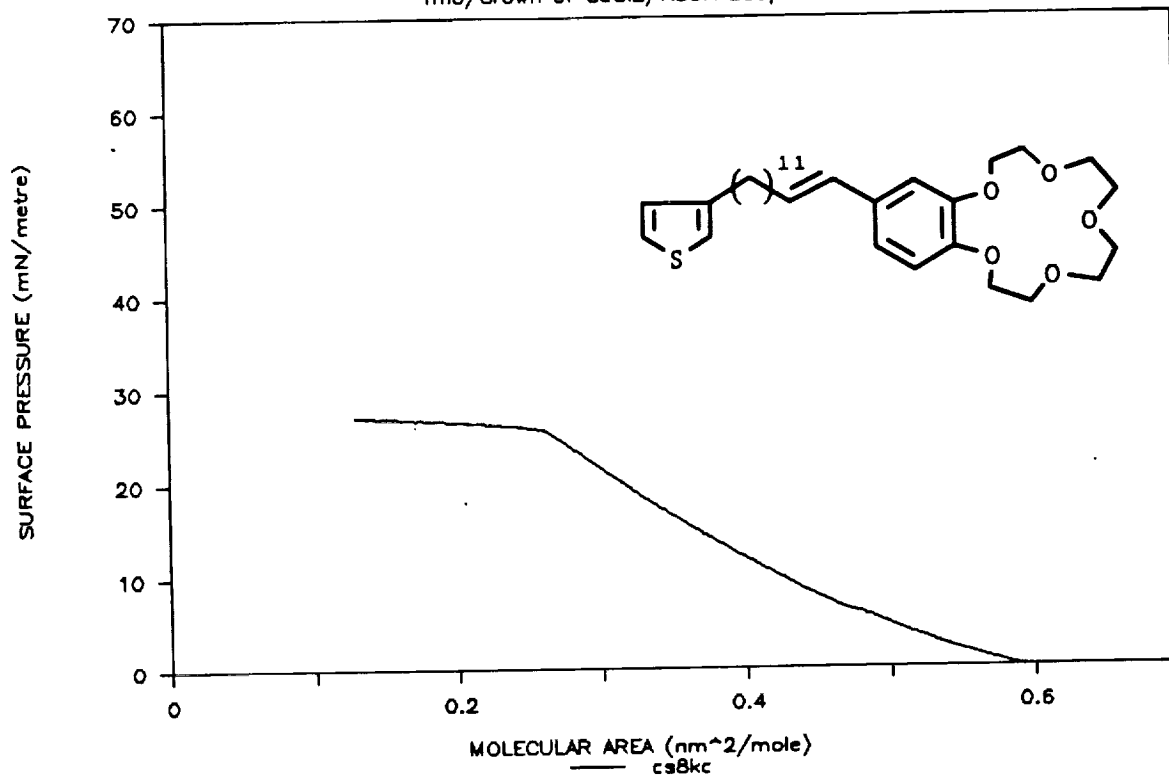
SURFACE PRESSURE vs. MOLECULAR AREA

Thio/Long-chain Crown on Pure Water

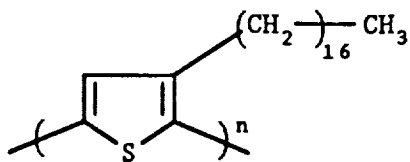


SURFACE PRESSURE vs. MOLECULAR AREA

Thio/Crown of CdCl₂/NaOH Subphase



Compound Z

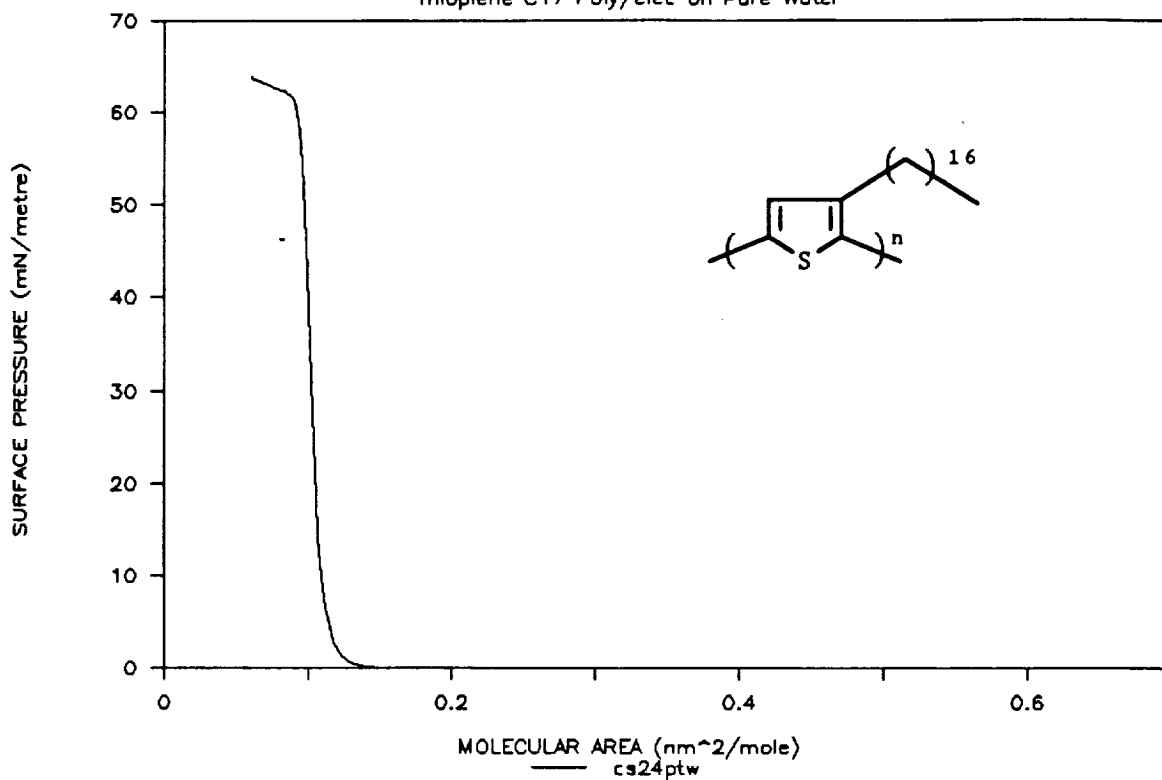


7

Compound Z is the result of electropolymerization of compound 5. Isotherm data shows that some type of film formation is taking place. The subphase has little to do with the film formation. The film that is formed must be layered due to the low molecular area achieved. The structure may be a bilayered formation inherent to the polymer's structure.

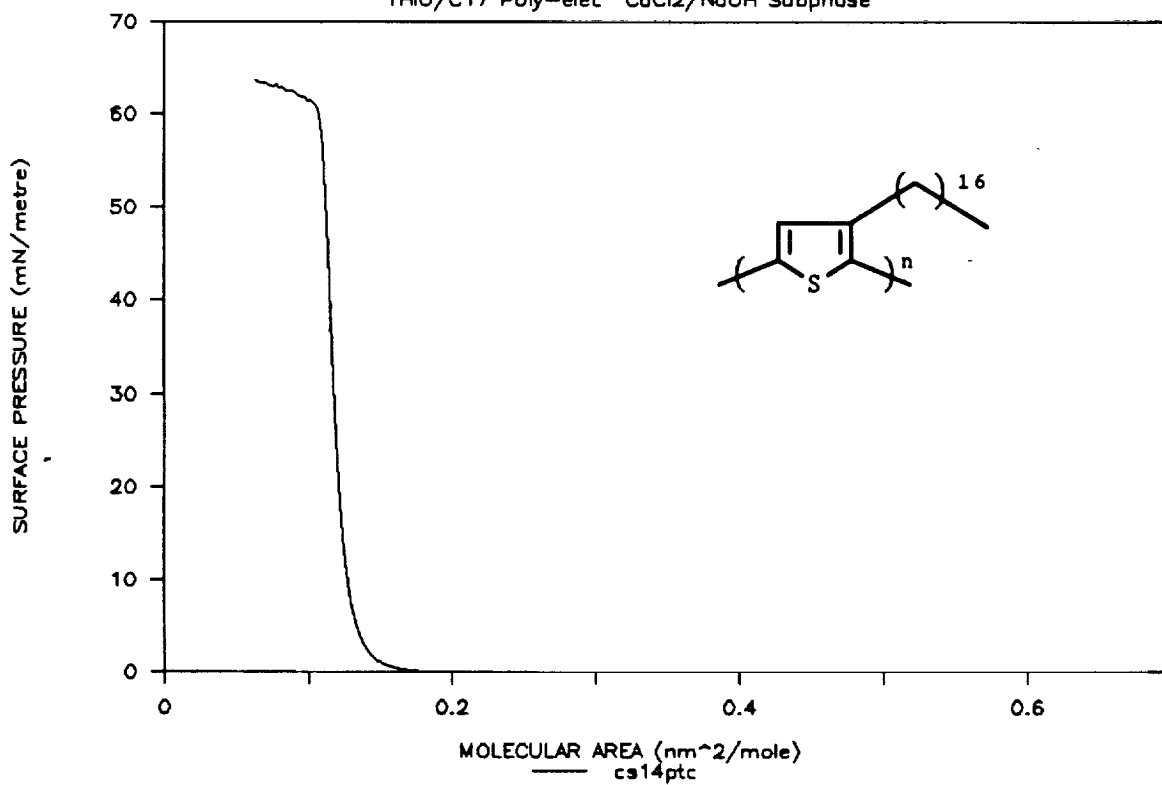
SURFACE PRESSURE vs. MOLECULAR AREA

Thiophene C17 Poly/elec on Pure Water



SURFACE PRESSURE vs. MOLECULAR AREA

THIO/C17 Poly-elec CdCl₂/NaOH Subphase



Film Deposition Studies:

Film Deposition of Compound 1:

Since 1, 2, and 4 seemed to form L-B films, these materials were candidates for film deposition. Compound 1 was the first material tried. A five minute creep test was performed to test the stability of the film. (see page 17) On a prewetted glass slide, compound 1 was deposited in a 1:1 ratio (film surface area decrease surface area of the glass slide) resulting in one deposited monolayer This was allowed to dry for 1/2 an hour after which time a second and third layer were successfully deposited on the slide. Soon after this dipping cycle the film collapsed. A creep test documenting this collapse is shown The film was stable for approximately 3 minutes after the slide exited the trough. It became apparent that further stability/creep tests needed be performed. Optimization of the dipping process may lead to stable film deposition that may be further characterized.

Stability/creep tests of Compound 1:

A 4 hour creep test was performed on compound 1 the result of which is shown. Upon trying to repeat this creep test the film immediately collapsed due to a small overflow that was initially not observed. A standard creep test was performed on docosanoic acid /pure water system to insure that the L-B trough was working

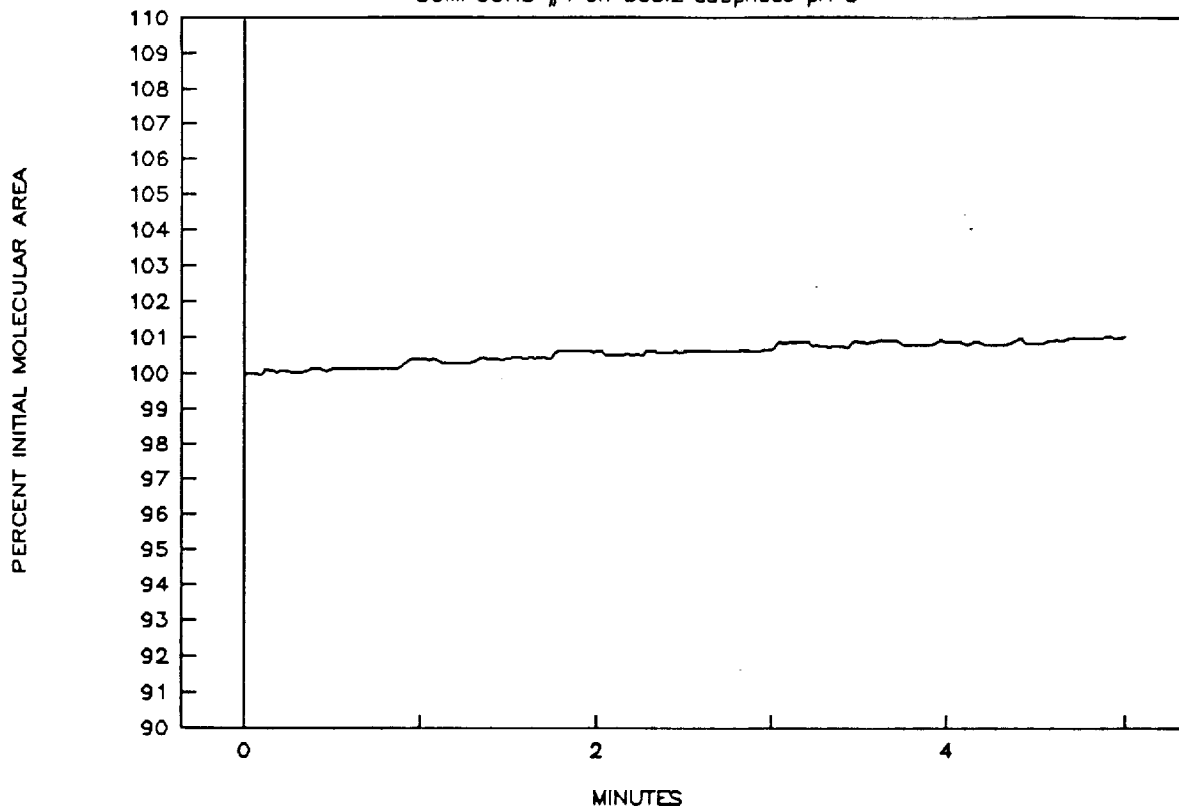
properly. The 20% area loss after 2 hours was, in the opinion of an experienced coworker, ok for that system. The trough was not leaking across the barrier since removal of collapsed material resulted in a surface pressure 0. With the time remaining I decided to test the effect of subphase pH on surface pressure vs. molecular area isotherms. Compound 1 was tested on a cadmium subphase at pH 7. This resulted in a bulk surface precipitation of the material. Due to the limited time available no further pH tests were performed.

Future Work:

The effect of subphase pH on surface pressure vs molecular area isotherm of compounds 1, and 4 need to be performed. Creep tests for compounds 1, 4 and 7 at optimal subphase pH. need to be performed. Also, as a result of isotherm analysis, certain structural modifications of the materials studied were hypothesized to hopefully bring about better L-B film formation. Those structural modifications include lengthening the alkyl chains of compounds 4 and 5. Also, new subphases may be tried for compound 6.

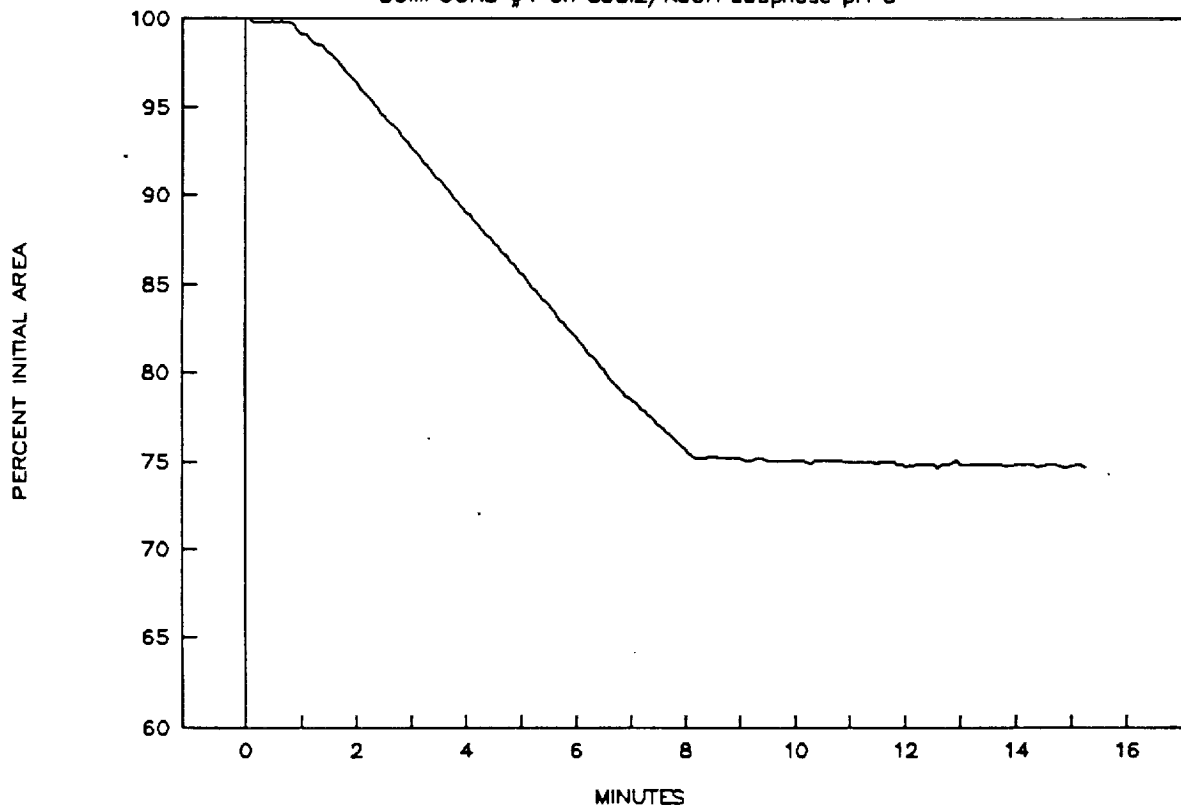
INITIAL CREEP TEST

COMPOUND #1 on CdCl₂ subphase pH 5



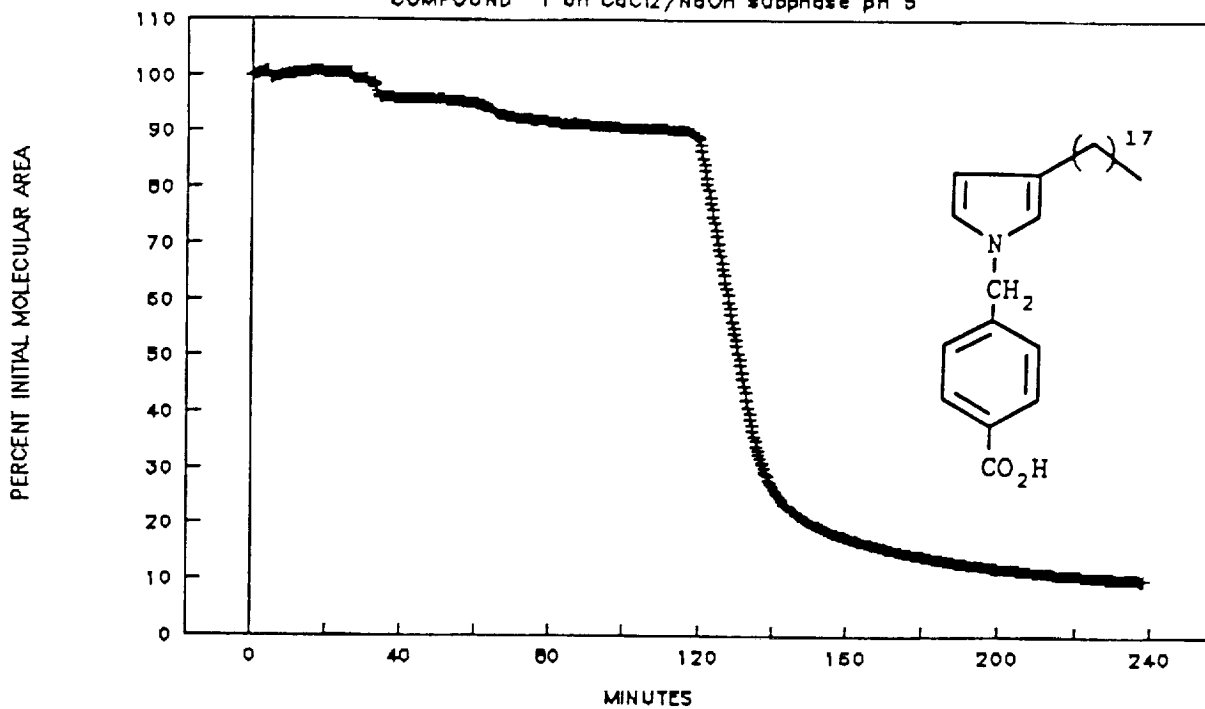
CREEP TEST AFTER A 2-WAY DIP CYCLE

COMPOUND #1 on CdCl₂/NaOH subphase pH 5



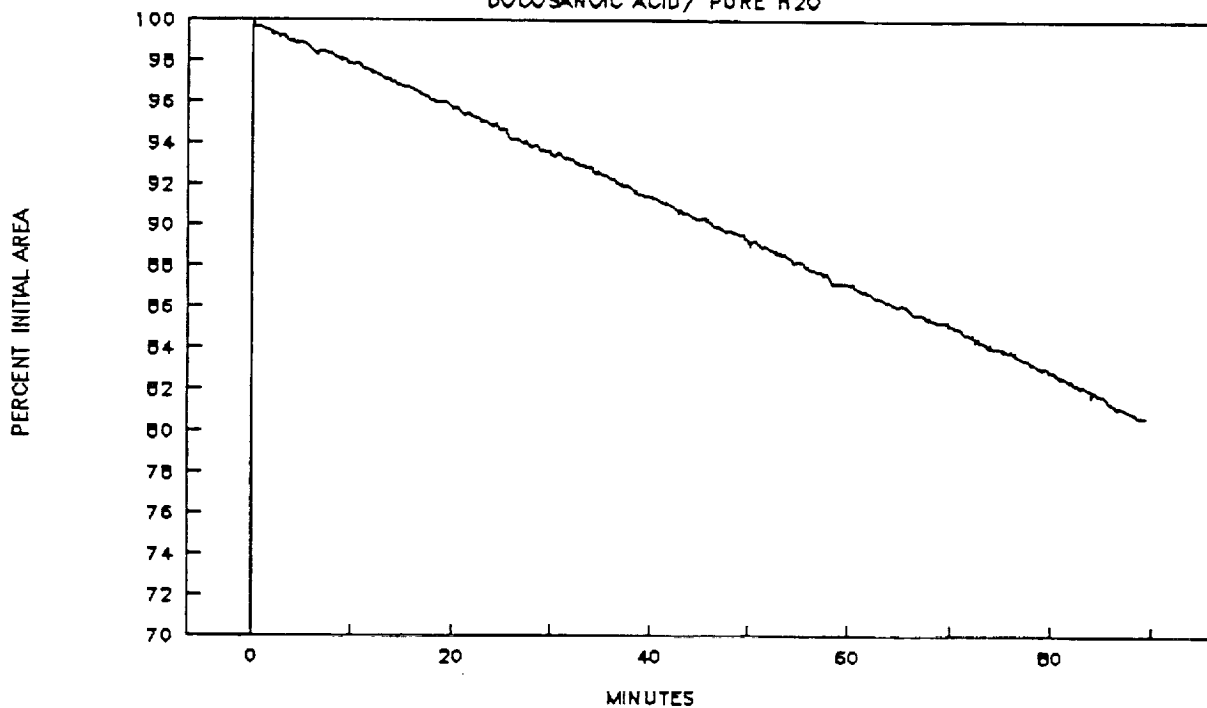
FOUR HOUR CREEP TEST

COMPOUND 1 on CdCl₂/NaOH subphase pH 5



CREEP TEST 90 MINUTES

DODOSANOIC ACID / PURE H₂O



45 a

Conclusions:

During the duration of this grant a number of novel 3-long-chain substituted thiophenes and furans were synthesized. Also preparative strategies have been developed to synthesize 1-substituted-3-long-chain substituted pyrroles, a class of compounds which was unknown before.

It was shown that the 3-long-chain substituted thiophenes can be polymerized. The films show a conductivity in the range of 10^{-1} S/cm.

One polymer was tested as a Langmuir-Blodgett film providing species and it showed, though not completely satisfactorily, formation of a Langmuir-Blodgett film.

Also, one of the novel pyrroles exhibited formation of a Langmuir-Blodgett film. On the strength of these very promising leads, good conducting Langmuir-Blodgett films could be developed. However, the time of the grant ran out before we were able to do this work.

Finally, preliminary work using pyrrole and 3-methylthiophene as monomers to coat Ga/As wafers showed promise. The research involving pyrrole gave strong indications that more in-depth research might give useful results (see Appendix for preliminary work with pyrrole and 3-methylthiophene).

The research done with financial aid from NASA was done by two postdoctoral assistants: Drs. Adel Amer and Rashad Shabana. It constitutes a major part of the Ph.D. thesis of Ms. Cynthia Striley (University of Cincinnati, 1994). So far, one paper has resulted: *A convenient synthesis of long-chain-3-n-alkylthiophenes and 3-n-alkylfurans*, with R. Shabana, A. Amer, H. B. Mark, Jr., Phosphorus, Sulfur and Silicon, 1990, 53:299-306.

Appendix I:

Protocol of Experiments Designed to Coat GaAs Wafers with a Polymer, with Pyrrole and 3-Methylthiophene as a Model Compound:

This protocol describes the results of a single and very preliminary experiment, therefore it is proposed to optimize conditions of the poly(pyrrol) film coating of the GaAs electrode by

- a. varying solvent and concentration of the monomer;
- b. by using a number of substituted pyrrol monomers;
- c. by varying the temperature.

It is further proposed to use different thiophene monomers and oligomers in order to achieve a coating of GaAs wafers with a conducting polymer. The experiments with thiophene based species seem to us important because according to our experience thiophene based polymers generally are more stable than pyrrole based ones. Again, the deposition of a film on GaAs wafers of a thiophene based polymer is likely to occur by simply changing the solvent.

It was anticipated that a majority portion of this research up to a point where it becomes evident whether the hoped-for application can be achieved could be done within a two year period; however, due to termination of grant this research, though very promising, could not be done.

Report of Polymer Studies at GaAs Electrode:

Purpose: In order to improve the performance of GaAs as an electrode in a photovoltaic cell, it is attempted to cover it with a polymer film.

Experimental Conditions:

1. **Electrode:** GaAs is Zn doped with carrier density of $5.5 \times 10^{18} \text{h}/\text{cm}^3$. It is a single crystal, cut between $\langle 100 \rangle$ and $\langle 110 \rangle$ ($400^\circ - 2.3^\circ = 410^\circ$), thickness 1100 μ . This GaAs wafer was provided by NASA.
2. **Electrolyte:** 0.5M NaClO_4 (GFS) in CH_3CN (HPLC grade, Fisher), deaerated by saturating CH_3CN with N_2 .
3. **Cell and Electrodes:** An electrochemical H cell is used. Auxiliary electrode is Pt wire and reference electrode is Ag/AgCl (1M NaCl).

4. Light Source: slide project and one focus lens.

Results:

1. Electrode Pretreatment: There are three ways to pretreat the electrode.
 - a. The originally obtained GaAs is first rinsed with H_2O and then CH_3CN .
 - b. After a) the electrode is rinsed with H_2O , then immersed in concentrated HF for 30-60 sec. followed by a rinse with CH_3CN .
 - c. The same as b) except a 1:1 H_2O_2/H_2SO_4 mixture was used as etching solution.

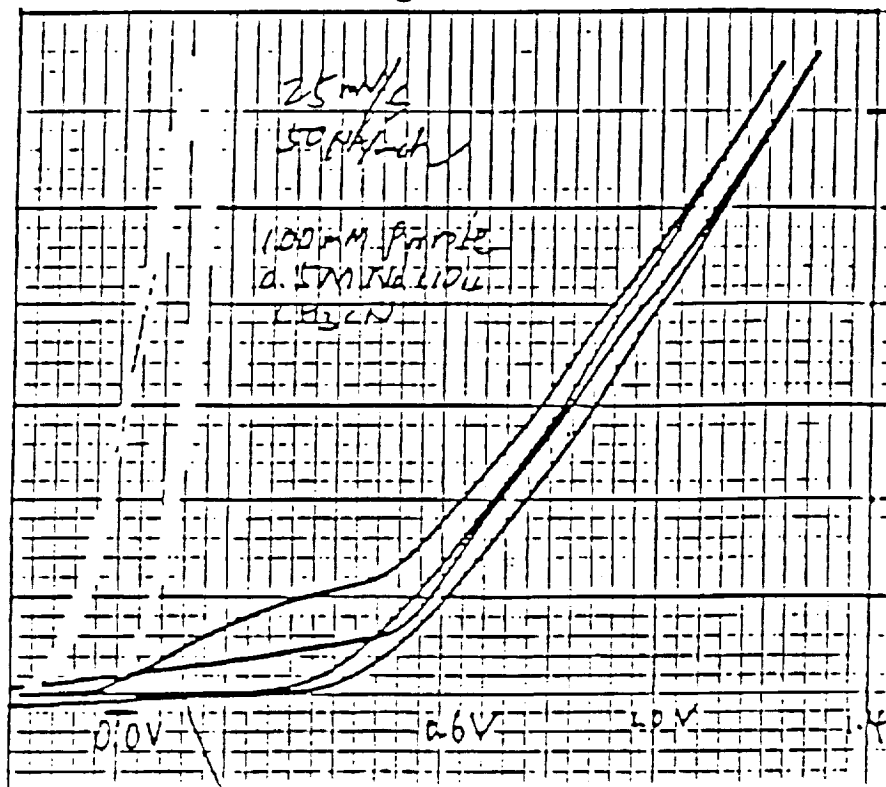
For a GaAs electrode covered by a layer of polymer, the electrode is washed with hot chromerge solution to remove polymer, then subjected to the above pretreatment.

From the experimental results, the pretreatment b (HF rinse) is the best choice because such pretreated electrodes are more conductive.

2. Pyrrole Polymer on GaAs

The HF treated electrode is immersed in 100 mm pyrrole solution, with light irradiation. Polymer formation took place below 1.2V. The cyclic voltammogram is shown below (Figure 1).

Figure 1:

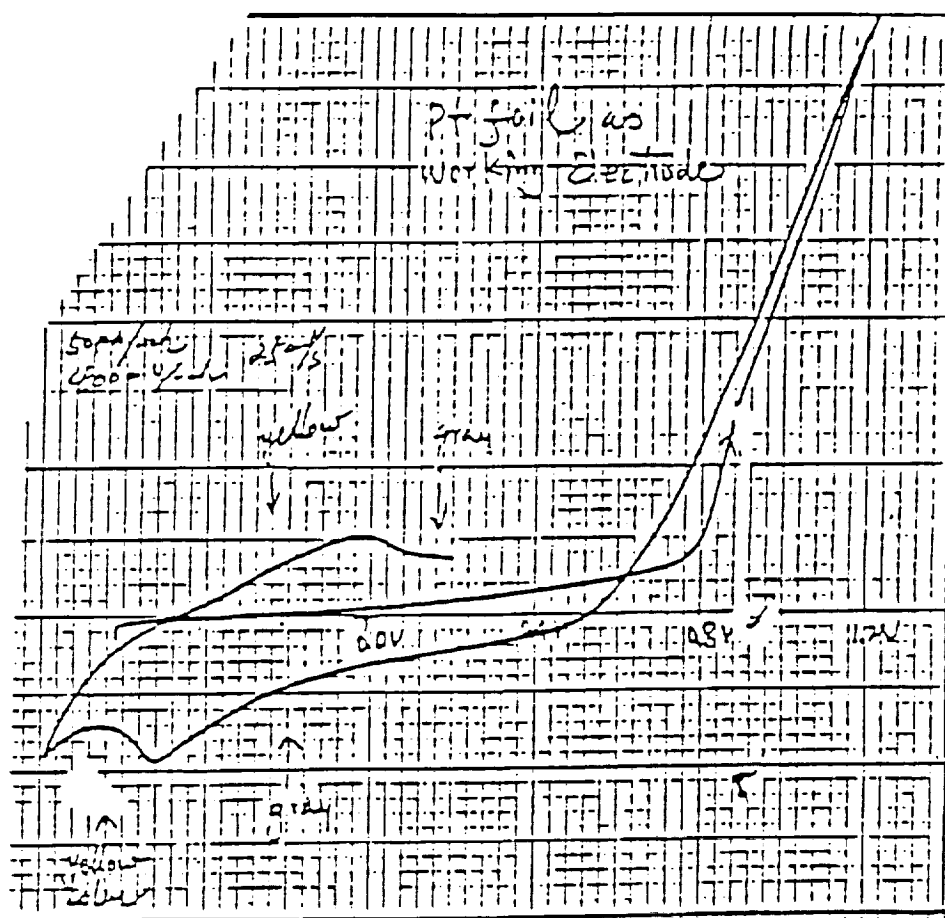


Without light irradiation no polymer formation was observed at the above described conditions. This is illustrated clearly by exposing only one side of the electrode to light. The result is polymer formation only on the side of the electrode which is irradiated.

For comparison, a pyrrole polymer is also formed on a Pt electrode. The polymer is more uniform than that on GaAs.

The redox peaks for the polymer on the Pt electrode can be easily obtained. This is illustrated in Figure II. This is quite different for the redox peaks obtained for the GaAs electrodes as is evident by comparing the CV's of Figure I and Figure II.

Figure II



3. 3-Methylthiophene Polymer on GaAs.

3-MTP polymer could not be formed on GaAs under conditions which permit formation of a useful 3-MTP polymer on a Pt surface. However, a polymer was formed at very positive potentials @ 2.8 V on GaAs but is not uniformly distributed on the electrode surface; it rather covered the surface only with some small spots.

Conclusions:

The above report is the brief summary of our preliminary investigation of polymer formation on GaAs. The experimental conditions are by no means optimized. The solvent, electrolyte, solute concentration, light source (frequency and intensity) and electrode pretreatment are also important factors in the polymerization process and have to be investigated. Pyrrole and its derivatives seem to be better candidates for formation of a film on polymer GaAs. When pyrrole polymerization is understood, we will be better prepared for investigations directed towards formation of films on GaAs surfaces.

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