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Benny D. Freeman, Assistant Professor

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
N.C. State University
Department of Chemical Engineering
Campus Box 7905
Raleigh, N.C. 27695-7905

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13. ABSTRACT *(Maximum 200 words)*

The objective of this research program was to develop and characterize new air separation membrane materials based upon polymers with tetradentate Schiff-base/Co(II) chelates incorporated in the chain backbone. Many tetradentate Schiff-base/Co(II) chelates can reversibly bind oxygen and could, therefore, act as sites for facilitated transport of oxygen through polymeric membranes. However, these compounds often undergo irreversible binding with oxygen, leading to performance deterioration over time. Blending small molecule Schiff-base/Co(II) chelates with polymers or using polymers as the axial ligands required to activate the Co(II) for oxygen binding results in a significant increase in the resistance of the compounds to undergo irreversible oxidation. This project explores the notion that the positive oxygen binding stability effects of combining Schiff-base/Co(II) chelates with polymers might be markedly improved by incorporating the oxygen-binding sites into the backbone of the polymer chain. We have found that polymers containing Schiff-base/Co(II) in the chain backbone were not very soluble and had, therefore, very low degrees of polymerization. Several novel Schiff bases were synthesized, and their oxygen binding characteristics were determined in solution. The program is continuing to determine the oxygen binding characteristics of these compounds when blended into conventional glassy polymers.

14. SUBJECT TERMS
new air separation membrane materials, facilitated transport of oxygen, tetradentate Schiff-base/Co(II) chelates, reversible oxygen binding

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REACTIVE POLYMERS: MAIN-CHAIN COORDINATION POLYMERS FOR AIR SEPARATION

FINAL REPORT

BENNY FREEMAN

APRIL 15, 1994

U.S. ARMY RESEARCH OFFICE

CONTRACT NUMBER DAAL03-89-D-0003

NC STATE UNIVERISTY
DEPARTMENT OF CHEMICAL ENGINEERING

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FOREWORD

This Foreword provides a brief history of a confluence of unusual events, outside the scope of the following technical discussion related to the progress achieved during the program, which have markedly affected the ability to execute the research program described in the original research proposal. This research program began as an ARO staff research project involving Dr. G. Ronald Husk (ARO) and Professor R.T. Chern (N.C. State University, Department of Chemical Engineering). Professor Chern left N.C. State University in 1991. At this time, Professor Benny D. Freeman (N.C. State University, Department of Chemical Engineering) took over the research project from Professor Chern. Subsequently, Dr. Husk took medical retirement from ARO in 1992 and, eventually, passed away from complications related to chronic renal failure. Professor Freeman worked with Dr. Bob Ghirardelli of ARO to bring ARO's involvement in the program to an end by November 30, 1993. Since this time, Professor Freeman and one Ph.D. graduate student, Mr. Suresh Sunderrajan, have continued work on this research program under sponsorship of the National Science Foundation.

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STATEMENT OF PROBLEM STUDIED

The objective of this research program was to develop and characterize new air separation membrane materials based upon polymers with tetradentate Schiff-base/Co(II) chelates incorporated in the chain backbone. Many tetradentate Schiff-base/Co(II) chelates can reversibly bind oxygen and could, therefore, act as sites for facilitated transport of oxygen through polymeric membranes. However, these compounds often undergo irreversible binding with oxygen, leading to performance deterioration over time. Mixing small molecule Schiff-base/Co(II) chelates with polymers or using polymers as the axial ligands required to activate the Co(II) for oxygen binding results in a significant increase in the resistance of the compounds to undergo irreversible oxidation. This project was proposed to explore the notion that the positive oxygen binding stability effects of combining Schiff-base/Co(II) chelates with polymers might be markedly improved by incorporating the oxygen-binding sites into the backbone of the polymer chain.

SUMMARY OF THE MOST IMPORTANT RESULTS

During the course of the program, four soluble polyimines, having Schiff base moieties in the chain backbone, were synthesized. Their chemical structures are presented in Table 1. These macromolecules were designed to be highly soluble in common organic solvents such as methylene chloride and THF. The molecular feature leading to enhanced solubility in the polymers in Table 1 is the inclusion of bulky cardo groups (phenophthalein and hexafluoroisopropylidene) in the chain backbone. These groups enhance solubility by disrupting interchain packing through the introduction of bulky molecular-level “kinks” into the chain structure.

The molecular weights of these polymers were found to be quite low. The source of the low molecular weights is believed to be due to inherently low solubilities of even low molecular weight oligomers prepared from monomers containing Schiff-base structures. While these materials are considerably more soluble than the analogous polymers without the bulky cardo groups, the solubility of the new materials is apparently not sufficient to allow synthesis of high molecular weight polymers. High molecular weight polymers are required to form strong films for membrane studies and applications.

Based on this result, the direction of the research program was changed. The principal objective of the program was to improve the oxygen binding stability of Schiff-base/Co(II) chelates. The benefits of incorporating the chelated materials in the polymer backbone are believed to be related to the low mobility associated with the glassy state of polymers. We have, therefore, directed our research efforts towards enhancing the oxygen binding and transport ability of common, amorphous glassy polymers by blending novel, small molecule Schiff-base/Co(II) chelates with these polymers. The polymers selected for this work include poly(methyl methacrylate) (PMMA) and polystyrene (PS). We have synthesized a series of new Schiff bases, described in one of the manuscripts listed later in this document. The chemical structure of two Schiff-bases, Salen and Acasalen, are presented in Table 2. Salen is a standard Schiff base, and Acasalen is one of the novel Schiff bases prepared in this study. Upon activation with cobalt and an axial base such as pyridine, such Schiff bases can bind oxygen. The synthesis effort has been directed towards making new Schiff bases which are soluble and bind oxygen reversibly when incorporated in polymeric matrices.

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The results presented in this report related to the characterization of the oxygen binding capability of the Schiff bases provide a perspective of the performance of these materials relative to a common standard, Salen. For brevity, only the characterization data for Acasalen are presented in this report. This compound is the best characterized of the novel Schiff bases developed in this program. More detailed characterization information for the other Schiff bases is available in the manuscript, which will be forwarded to ARO upon completion.

Experimental Protocol

Gravimetric kinetic sorption studies of the ability of Co(Salen) groups to selectively facilitate the absorption and diffusion of oxygen in glassy polymers were carried out. A model system, consisting of poly(methyl methacrylate) (PMMA) blended with Co(II) Salen is the first material being studied. The Co(II) Salen was blended with PMMA in a chloroform solution. This system was selected because PMMA is soluble in chloroform, Co(II)Salen is stable in chloroform, and the solvent is quite volatile, allowing the preparation of uniform thickness, thin, chloroform-free films. A 5μm thick film of this blend was cast from solution and dried in a vacuum oven. This film was suspended by a quartz microspring in a gravimetric sorption cell.

The atmosphere surrounding the film may be controlled. In a typical experiment, the film would be contacted with pyridine vapor at a fixed activity of pyridine. (Activity in these experiments is defined as the ratio of the partial pressure of pyridine to it's vapor pressure. For the studies reported herein, a pyridine activity of 0.3 was used.) Some of the pyridine sorbed into the film binds to free coordinating sites of the cobalt in the Co(II)

Schiff base chelate and acts as an axial ligand. This process activates the cobalt complex for oxygen binding. The weight gain of the film, associated with the sorption of pyridine into the film, is recorded as a function of time until no more pyridine was absorbed by the film, indicating that the system was at equilibrium. Then the film is exposed to oxygen, and the weight of the film is monitored as a function of time. These results are compared to sorption curves for oxygen in a comparable film without the Co(II) Schiff base complex. Any excess oxygen sorption in the first case is ascribed to oxygen binding to the Co(II) Schiff base complex. These experiments can, therefore, provide a direct probe of the oxygen absorption capability of pyridine-activated Co(II)Salen moieties.

Gravimetric Sorption Results

A series of gravimetric sorption experiments were performed using Co(II)-Salen and Co(II)-Acasalen as the fixed-carriers, pyridine as the axial ligand, and polymethylmethacrylate (PMMA) and polystyrene (PS) as matrix polymers.

Figure 1 presents sorption and desorption curves for pyridine sorption in a PMMA film containing 20% Co-Salen by weight. At time=0, the polymer film, which had been degassed in vacuum, was contacted with pyridine, and the increase in film weight is associated with the absorption of pyridine by the polymer film. After 120 min$^{1/2}$ (approximately 10 days), the pyridine was evacuated from the atmosphere surrounding the film, and the film weight decreased as pyridine desorbed from the film. Even upon protracted desorption, the pyridine cannot be completely removed from the film, as indicated by the desorption curve, which never returns to zero. The amount of pyridine left in the film (approximately 13 weight percent in the example presented in Figure 1) is well in excess of the weight of sorbed pyridine associated with activation of all of the Co(II) Schiff base sites. This result, complemented by a careful FT-IR study, led to the conclusion that pyridine appears to undergo favorable interactions with PMMA and that, under normal conditions in the gravimetric sorption experiment, complete removal of the pyridine from the polymer was not achieved.

The study of the facilitation capability of Co(II) Acasalen was executed by changing the matrix polymer to polystyrene to eliminate the favorable interaction between pyridine and the carbonyl linkages in PMMA. Figure 2 presents representative gravimetric sorption data for the sorption of pyridine into a film containing 5 weight percent Co(II) Acasalen. The sorption kinetics are well described by a Fickian sorption model; however, pyridine again does not completely desorb, as indicated by the non-zero value of pyridine sorption at extremely long times. The amount of pyridine left in the film is thought to be attached to the Co-Schiff base complex. From the amount of pyridine actually left within the film we calculate the fraction of Co(II)-sites present that are activated (i.e. those that have reacted with pyridine and may bind an oxygen molecule). Assuming that one pyridine molecule binds to one Co-Acasalen molecule, the maximum amount of bound pyridine remaining within the film is 1.3 mg pyridine/100 mg of film. From the desorption data presented in Figure 2, 0.7 mg pyridine /100 mg of film is left in the film after desorption, corresponding to the activation of approximately 54\% of Co-sites within the film. This corresponds to a maximum oxygen sorption of 0.26 mg /100 mg of film. Experimental oxygen sorption values are well in excess of this value as shown in Figure 3.

The experimental procedure involves introducing pyridine into the sorption chamber and maintaining it at a constant activity until the sorption is complete. In order to expose the film in the sorption chamber to oxygen, oxygen maintained at 750 torr in a reservoir connected to the sorption chamber is allowed to expand adiabatically into the chamber, without degassing the chamber beforehand. Within the sorption chamber is a mixture of pyridine at the specified activity and oxygen at 460 torr. The process of expanding oxygen into the sorption chamber, which happens over approximately one minute, results in the expansion of the gas from an initial pressure of 750 torr to a final pressure of approximately 460 torr.

Figure 3 presents an oxygen sorption curve for a film containing 20% Co-Acasalen/PS/pyridine. A maximum is observed in the gravimetric sorption data before the sorbed weight drops with time. A possible explanation for this result is related to Joule-Thompson cooling of the oxygen/pyridine mixture as it enters the gas sorption chamber. For a diatomic gas such as oxygen, a pressure decrease from 750 torr to 460 torr results in a corresponding temperature decrease from 308 K to 267 K (assuming ideal behavior). Pyridine activity is quite sensitive to temperature during oxygen expansion since pyridine vapor pressure depends exponentially on temperature. A temperature decrease of the order of 10°C is sufficient to increase pyridine activity by almost 50% (from 0.3 to 0.445). Though we are unable to measure the exact temperature decrease in the cell upon oxygen expansion, some local cooling of the gas mixture should occur. This temperature decrease substantially lowers the saturation vapor pressure for pyridine within the sorption chamber, which, in effect, increases the activity of pyridine in the chamber. As a result, more pyridine is sorbed by the film until the temperature again equilibrates within the chamber. Once the temperature equilibrates the excess pyridine within the film desorbs and the film attains a new steady weight corresponding to the weight of the pyridine as well as the weight of the oxygen sorbed. Experiments performed to date were stopped too early to observe the equilibrium uptake of oxygen in the presence of pyridine at a fixed temperature. In the future, the time scale of observation of oxygen sorption will be markedly extended to capture the equilibrium uptake of oxygen inthe film.

Pyridine which is not desorbed upon protracted exposure to vacuum may be the fraction of sorbed pyridine bound to Co(II) Schiff base molecules in the film. This fraction of pyridine is no longer in a 'free' state but remains in the membrane bound to the cobalt complex. We plan to study the sorption of oxygen into membranes which have been subject to pyridine sorption and desorption to determine if pyridine which remains in the film contributes towards Co(II) Schiff base activiation for facilitated oxygen transport. We also propose to use a less volatile axial base for gravimetric sorption in order to get around the difficulties we have had with sorption runs thus far.

Ultraviolet Spectroscopy Results

Ultraviolet (UV) spectroscopy provides a convenient method to characterize the incorporation of cobalt into the Schiff base, the binding of the axial ligand to the cobalt-Schiff base complex, and the binding of oxygen to the activated cobalt-Schiff base complex. Therefore, a series of UV spectroscopic runs were conducted on samples of Acasalen, Salen and Pphsalen (polyphenolphthalein-salen) dissolved in chloroform. A Shimadzu-2000 UV-Vis spectrophotometer was used to characterize the interaction between oxygen and Co-Schiff base complex in solution. An extended-neck cuvette with a glass-stopper was constructed. This enabled us to bubble gas through the solution within the cuvette and monitor in situ any changes in the spectrum of the solution. The experimental procedure involved preparing solutions of the appropriate concentration of Schiff-base , pyridine, and Co-acetylacetonate in the same solvent. The solvent used was chloroform. Successive spectra were taken for the

- Schiff-base solution.
- Schiff-base solution with Co(II).
- Co-Schiff base solution with pyridine. Nitrogen is bubbled through each of the solutions to insure that premature oxidation of the Co-Schiff base does not occur.
- solution containing Co-Schiff base and pyridine after bubbling oxygen through the solution.
- solution containing Co-Schiff base and pyridine after successively bubbling oxygen and then nitrogen. Oxygen and nitrogen continued to be successively bubbled through the solution and each time a spectrum was taken until there was no further change in peak position.

The above experimental procedure typically led to the following results:

- The appearance of a peak ca. 385 nm on addition of cobalt, pyridine and oxygen to a solution of Acasalen. This is taken as evidence of the reaction between Co-Acasalen and oxygen in the presence of pyridine as shown by Nishide et al.

- The disappearance of this peak when the solution is saturated with nitrogen showing that the bond between Co-Acasalen and oxygen is reversible.

- The reversibility is, however, only partial with the peak becoming stationary on exposure to oxygen and nitrogen for three or more successive cycles, a result of the irreversible oxidation of the complex. This is a result of the high affinity of Co(II)-Schiff base complexes for oxygen when in solution.

- The peak shifts are more easily observed when the experiment is done at a reduced temperature, the reason being that the reduced temperature slows down the reaction rate and prevents the complex from getting irreversibly oxidized as quickly.

Discussion and Conclusions

Figure 4 presents a series of spectra for a 5×10^{-5} M solution of Acasalen in chloroform at room temperature. The appearance of new peaks on adding first cobalt and then pyridine to this solution is ascribed to binding between the Schiff-base and cobalt and then pyridine. Figure 5 presents UV spectra obtained on successively bubbling oxygen and nitrogen through the same solution. Curve 1 corresponds to the curve for Acasalen+Co+pyridine in Figure 4. Curve 2 represents the spectrum observed on bubbling oxygen through the solution; Curve 3 represents the spectrum upon bubbling nitrogen through the solution after obtaining Curve 2. The other even numbered curves, 4 and 6, represent the spectrum obtained upon repeated exposure of the solution to oxygen, while Curve 5 represents the spectrum obtained on exposure to nitrogen between oxygen exposures. After Curve 6, no measureable changes were observed in the spectrum upon repeated successive exposures of the solution to oxygen and nitrogen.

Nitrogen was bubbled through this solution to ensure that no premature oxidation of the Co-Schiff base occured. Curve 2 shows the shift in the peak position on bubbling oxygen through the solution. This increase in absorption of the band centered at about 388 nm is ascribed to the binding of oxygen to pyridine-activated Co-Acasalen. On further bubbling nitrogen through this solution, the peak almost returns to its original position. Some of the Co-Acasalen is probably irreversibly oxidized, explaining why Curve 3 does not coincide with Curve 1. The peak appears and disappears respectively, on successively bubbling oxygen (Curve 4), then nitrogen (Curve 5) and finally oxygen again (Curve 6). Each time the solution is exposed to oxygen, more of the Co-Acasalen present in the solution is presumably irreversibly oxidized and no longer participates in the binding reaction with oxygen.

Figure 6 presents the same series of spectra for a 5×10^{-4} M solution of Poly(phenolphthalein-salen) (Pphsalen) in chloroform. Pphsalen corresponds to polymer C in Table 1. These spectra were also obtained at room temperature. In this case, after the first cycle of bubbling nitrogen and oxygen (Curves 3 and 4, respectively), the shift in absorbance for successive curves (5, 6, 7 and 8) is very weak. Again this phenomenon is attributed to the irreversible oxidation of the Co-Schiff base complex.

The oxidation of the Co-Schiff base complex in chloroform appears to be, therefore, largely irreversible at room temperature. For this reason, we tried to obtain the same spectra at a reduced temperature (approximately

5°C) to reduce irreversible oxidation. Figure 7 presents several low temperature UV spectra obtained using Co-Acasalen dissolved in chloroform. The appearance (Curves 2 and 4) and disappearance (Curves 1 and 3) of the peak at 384 nm is pronounced. Curve 1 presents the spectrum for a 1×10^{-5} M solution of Acasalen in chloroform containing cobalt and pyridine. On contact with oxygen a new peak at 384 nm is observed in the solution spectrum (Curve 2). This peak disappears on bubbling nitrogen through the solution (Curve 3). It reappears on bubbling oxygen through the solution once again (curve 4). Further cycles did not produce any changes in the spectrum.

Figure 8 presents a reduced temperature UV spectrum of a solution of Co-Acasalen in chloroform at a somewhat lower Acasalen concentration (8×10^{-6} M). In this figure, Curve 1 represents the spectrum for Acasalen in chloroform. Curve 2 represents the spectrum after adding cobalt to the solution of Acasalen in chloroform. Curve 3 represents the spectrum upon adding pyridine to this solution. The change in the spectrum is ascribed to binding of the cobalt and Schiff-base, followed by binding of pyridine to the Co-Schiff base complex. On bubbling oxygen through the solution a new peak is observed around 388 nm (Curve 4). This peak vanishes (Curve 5) on bubbling nitrogen indicating that the reaction is reversible. The peak reappears when oxygen is bubbled through the solution once again (Curve 6). The apparent drift in the spectra is the result of changes in solution concentration within the cuvette due to vigorous bubbling of oxygen and nitrogen through the solution. From the composite results presented in Figures 7 and 8, it appears that the reversibility of oxygen binding of the activated aCo-Schiff base complex in solution is not strongly affected by Acasalen concentration.

In conclusion, UV spectroscopy at approximately 5°C does not render the binding between oxygen and cobaltous Schiff base complexes completely reversible in chloroform solution. However, UV spectroscopy appears to be sufficiently sensitive to obtain quantitative information regarding equilibrium constants for the reaction between oxygen and the Co-complex. We are currently using a jacketed cuvette to better control the temperature as well as using flow-meters to calculate the amount of gas flowing through the cell. We plan to perform UV spectroscopy of polymer films containing Co(II)-Schiff base complexes. In the solid state these complexes are known to be much less reactive and thus, less susceptible to irreversible oxidation. In fact, this is one of the most important reasons to pursue the development of films containing these complexes for air-separation applications. If the compounds were less susceptible to irreversible oxidation , longer lifetimes of the materials in actual service conditions would be obtained.

LIST OF ALL PUBLICATIONS AND TECHNICAL REPORTS

Guo, R.K., R.T. Chern, B.D. Freeman, and R.G. Husk, "Synthesis of Polyimines Having N,N'-Ethylene-bis(salicylideneimino) and Cardo Groups in the Main Chain," manuscript to be submitted to *J. Polym. Sci., Chem. Ed.*

Guo, R.K., R.G. Husk, R.T. Chern, and B.D. Freeman, "The Effect of Substituents on Solubility and Oxygen Binding Capacity for Cobalt(III) Chelated Salicylideneimine Derivatives," manuscript to be submitted to *Inorganic Chem.*

LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL

Mr. Suresh Sundarrajan, Ph.D. Candidate, Expected Graduation Date: 1995.

Dr. Rong-Kon Guo, Postdoctoral Fellow, 12/91 to 8/93.

Dr. G.R. Husk, ARO Scientist and Program Monitor (deceased).

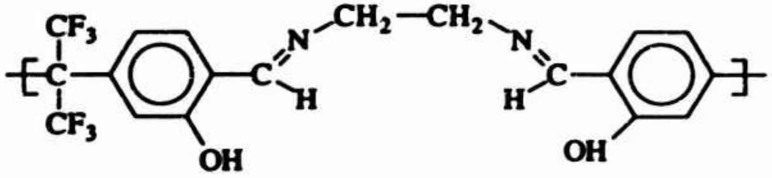
Professor Rey T. Chern, NC State University Assistant Professor.

Professor Benny D. Freeman, NC State University Assistant Professor.

TABLE 1

POLYMERS SYNTHESIZED DURING PROGRAM

A:



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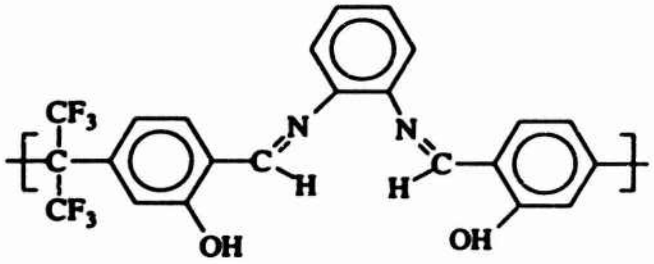

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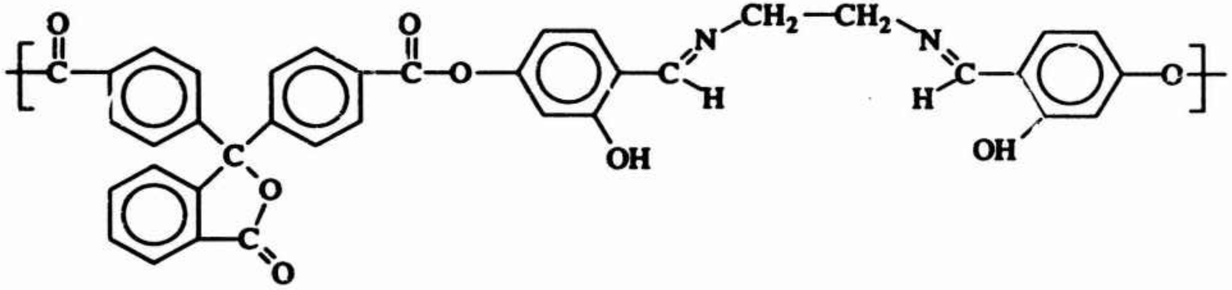

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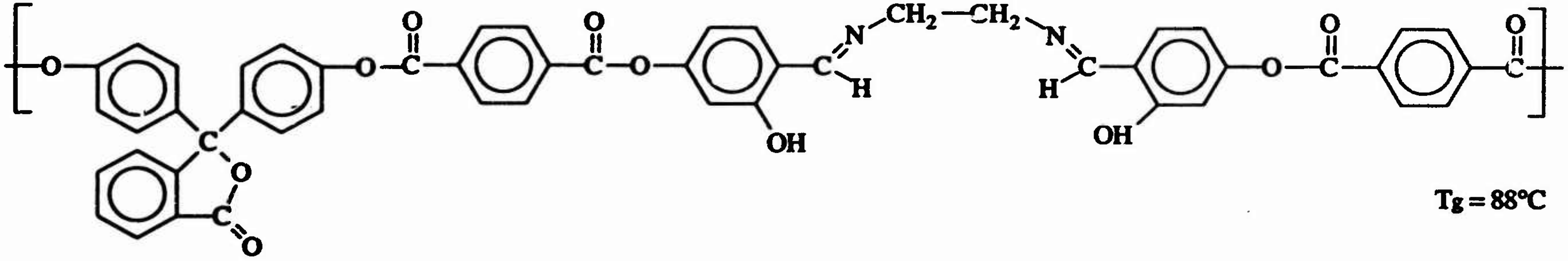
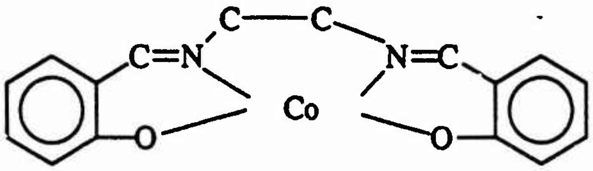
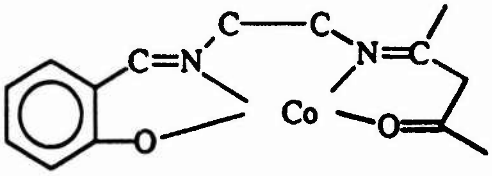


$T_g = 88°C$

Table 2: Schiff Base Chemical Structure



Co(II)Salen



Co(II) Acasalen

Schiff base structures are presented with cobalt already incorporated into the compound

Figure 1: Pyridine Sorption into a Poly(methylmethacrylate) Film Containing 20 Weight Percent Co-Salen

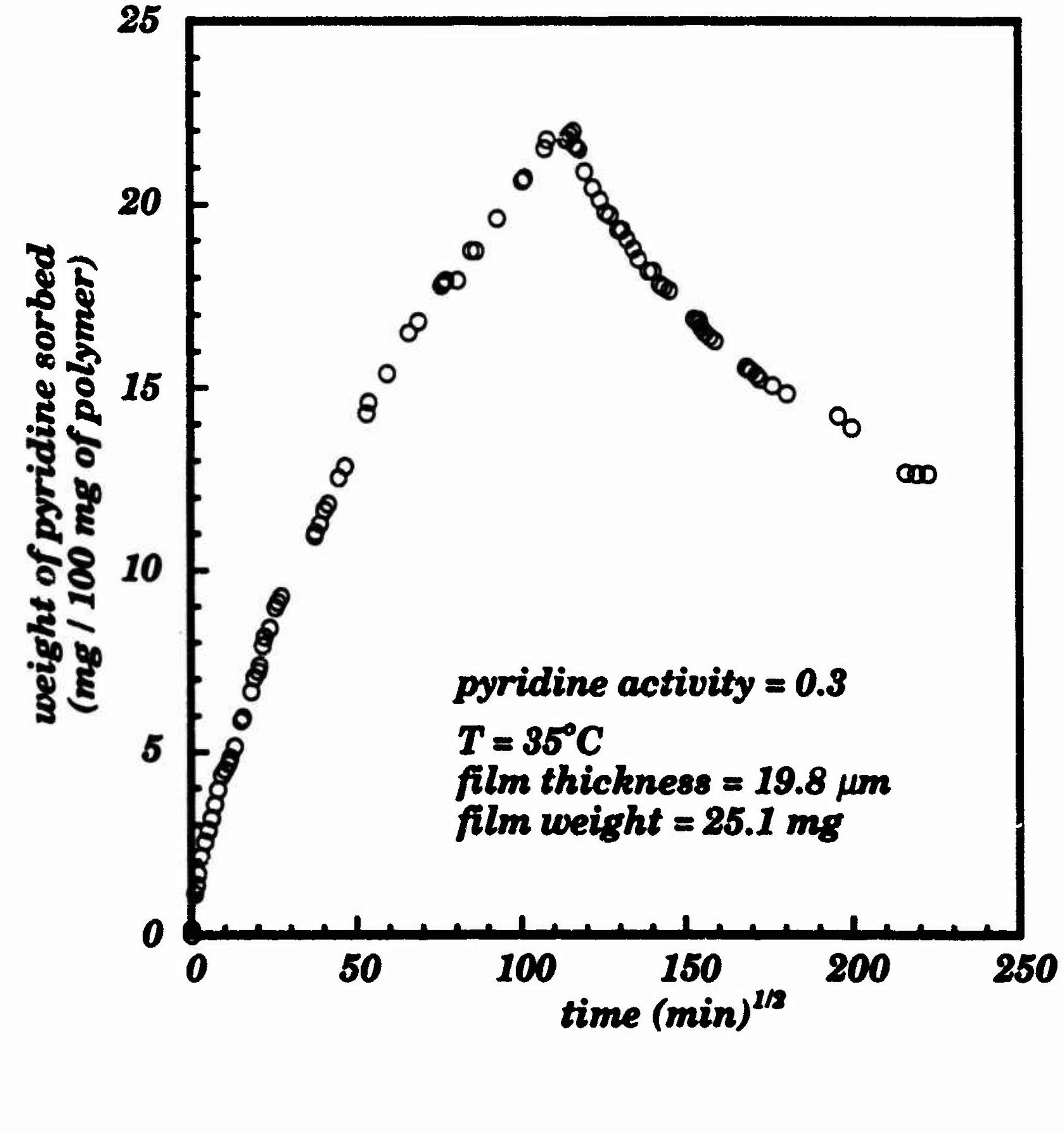


Figure 2: Pyridine Sorption into a Polystyrene Film Containing 5 Weight Percent Co-Acasalen

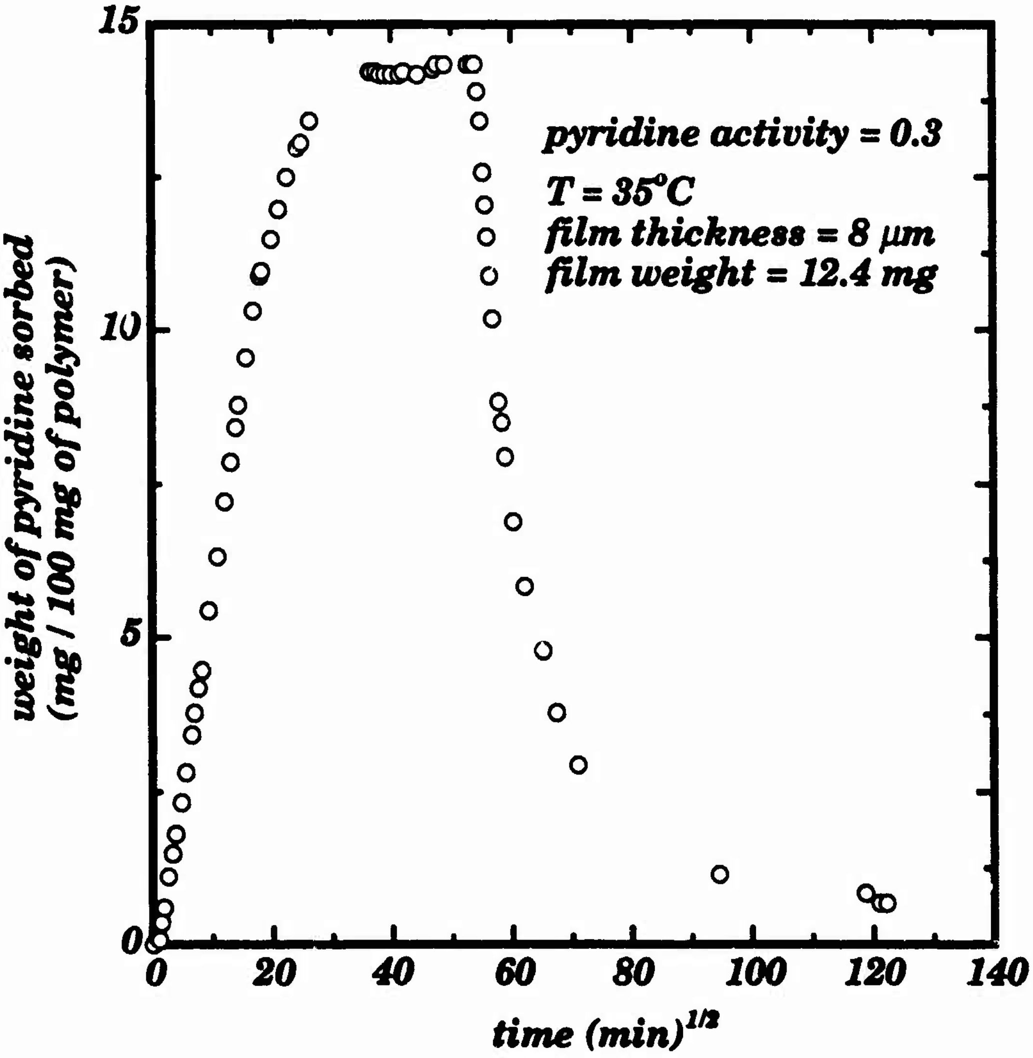


Figure 3: Oxygen Sorption into a Polystyrene Film Containing 20 Weight Percent Co-Acasalen

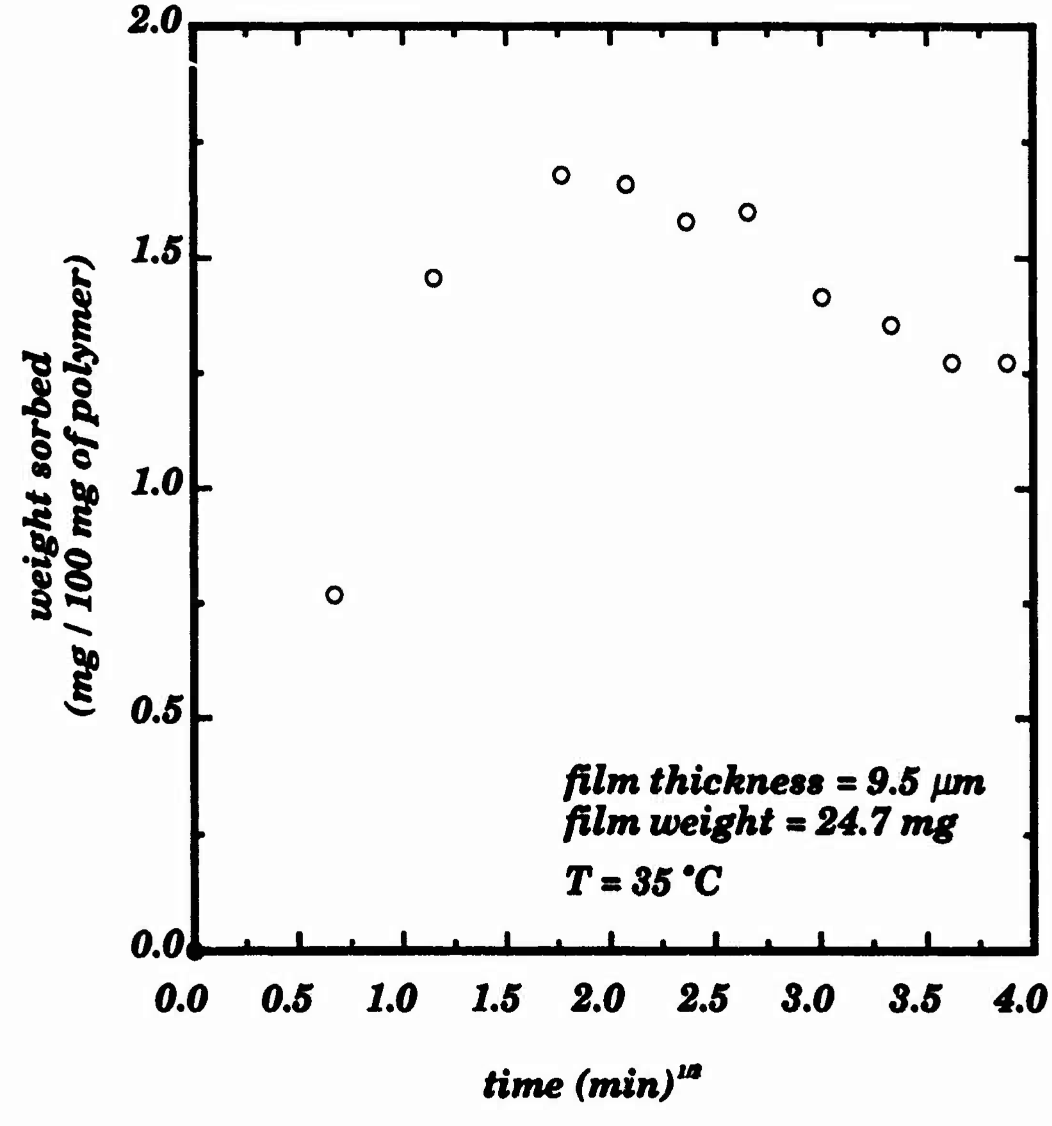


Figure 4: UV spectra of Co-Acasalen and Related Compounds in Chloroform

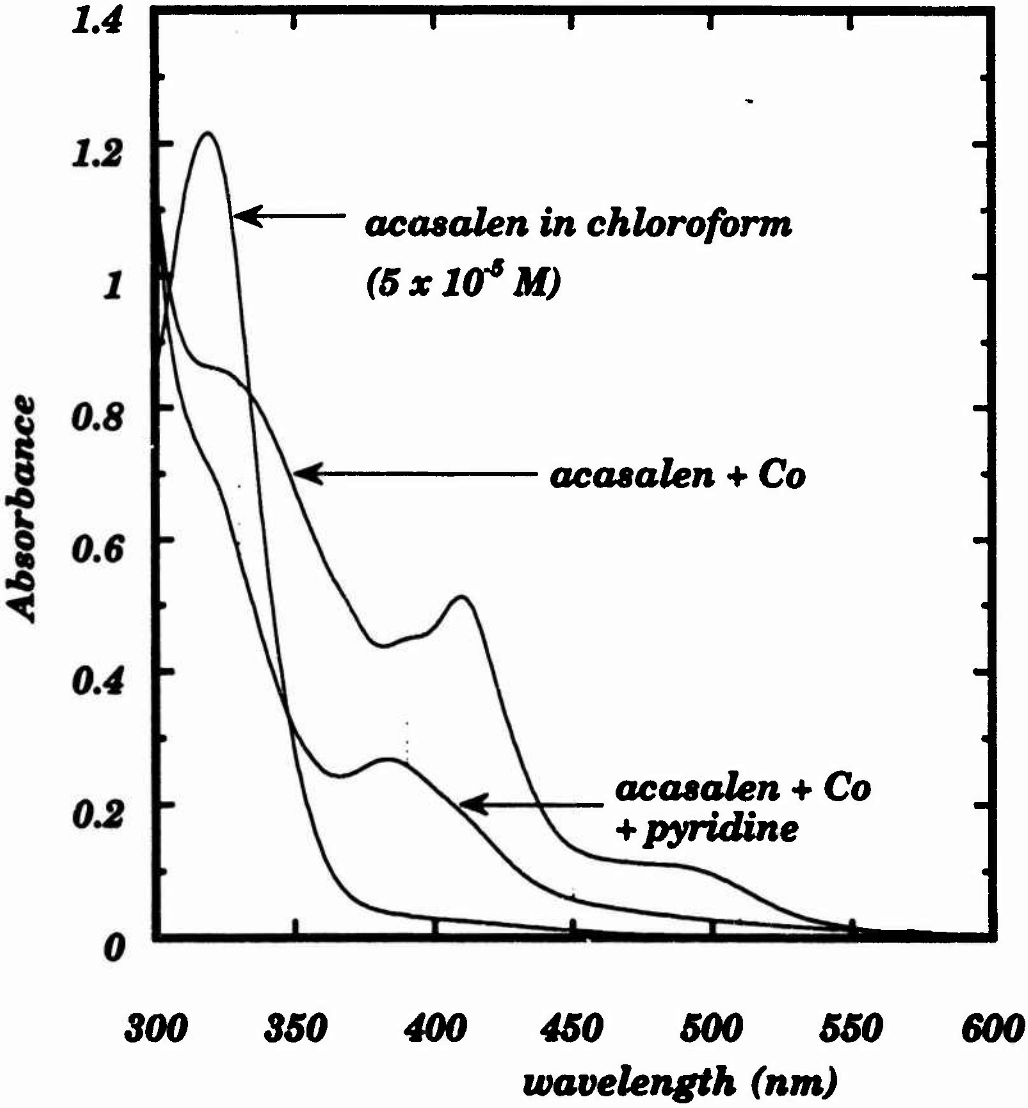


Figure 5: The Effect of Sucessive Oxygen and Nitrogen Contact on the UV spectra of Pyridine-Activated Co-Acasalen in Chloroform

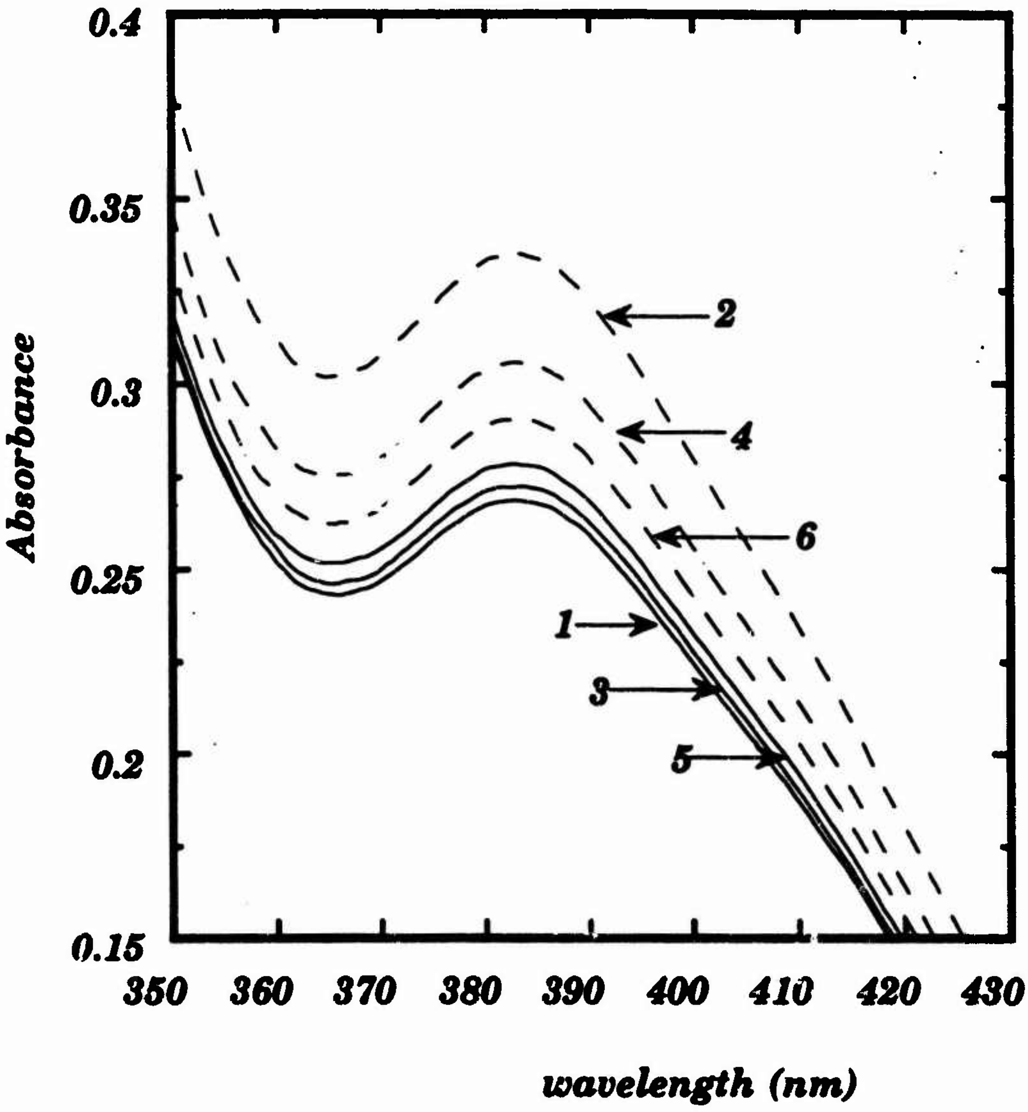


Figure 6: The Effect of Sucessive Oxygen and Nitrogen Contact on the UV spectra of Pyridine-Activated Co-poly(phenolphthalein-salen) in Chloroform

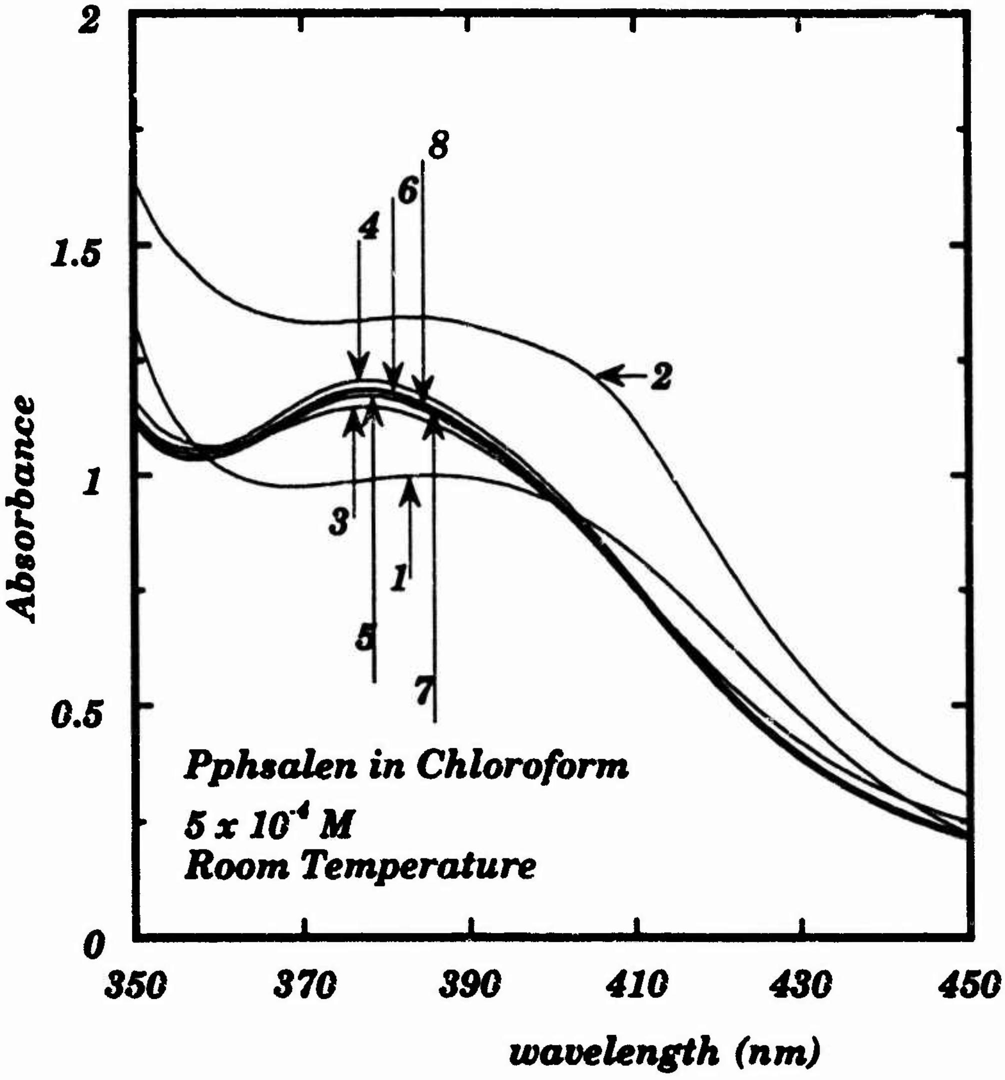


Figure 7: The Effect of Sucessive Oxygen and Nitrogen Contact on the UV spectra of Pyridine-Activated Co-Acasalen in Chloroform at Reduced Temperature

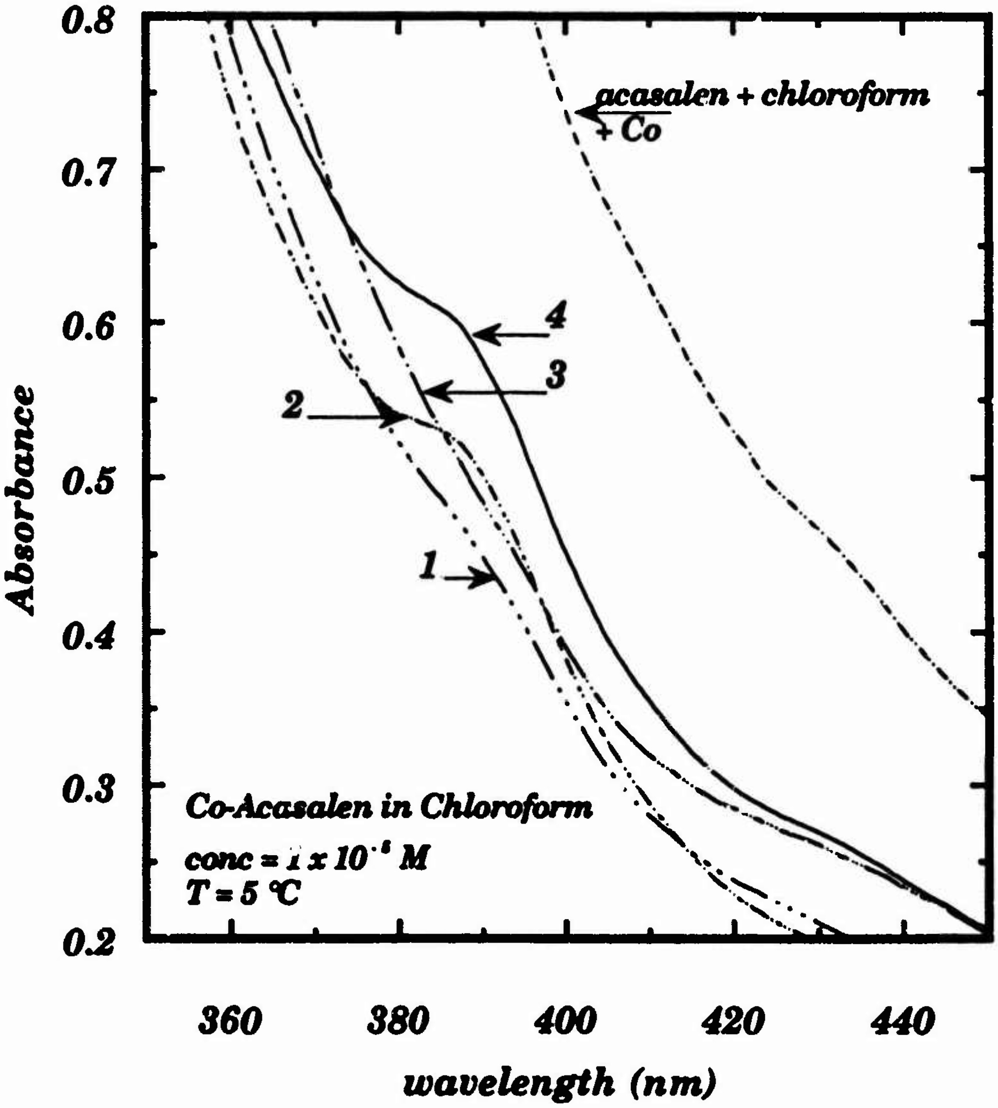


Figure 8: The Effect of Sucessive Oxygen and Nitrogen Contact on the UV spectra of Pyridine-Activated Co-Acasalen in Chloroform at Reduced Temperature and Reduced Co-Acasalen Concentration