

AD-A249 746



2

OFFICE OF NAVAL RESEARCH

Contract N00014-82K-0612

Task No. NR 627-838

TECHNICAL REPORT NO. 67

Infrared Investigations of Pristine Polypyrrole - Is the Polymer  
Called Polypyrrole Really Poly(Pyrrole-Co-Hydroxypyrrole)?

by

Junting Lei and Charles R. Martin

Department of Chemistry  
Colorado State University  
Ft. Collins, CO 80523

Prepared for publication

in

Synthetic Metals

April 30, 1992

DTIC  
S ELECTE D  
MAY 11 1992  
D

Reproduction in whole or part is permitted for  
any purpose of the United States Government

\*This document has been approved for public release  
and sale; its distribution is unlimited

\*This statement would also appear in Item 10 of Document  
Control Data - DD Form 1473. Copies of form  
Available from cognizant contract administrator

## REPORT DOCUMENTATION PAGE

Form Approved  
OMB No 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS			
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT APPROVED FOR PUBLIC DISTRIBUTION, DISTRIBUTION UNLIMITED.			
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE						
4. PERFORMING ORGANIZATION REPORT NUMBER(S)  ONR TECHNICAL REPORT #67			5. MONITORING ORGANIZATION REPORT NUMBER(S)			
6a. NAME OF PERFORMING ORGANIZATION Dr. Charles R. Martin Department of Chemistry		6b. OFFICE SYMBOL (if applicable)		7a. NAME OF MONITORING ORGANIZATION  Office of Naval Research		
6c. ADDRESS (City, State, and ZIP Code) Colorado State University Ft. Collins, CO 80523			7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (if applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER  Contract # N00014-82K-0612		
3c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217			10. SOURCE OF FUNDING NUMBERS			
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Infrared Investigations of Pristine Polypyrrole - Is the Polymer Called Polypyrrole Really Poly(Pyrrole-Co-Hydroxypyrrole)?						
12. PERSONAL AUTHOR(S) Junting Lei and Charles R. Martin						
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) 1992, 4, 30		15. PAGE COUNT
16. SUPPLEMENTARY NOTATION						
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)  conductive polymers, synthetic metals, electronic conductivity			
FIELD	GROUP	SUB-GROUP				
19. ABSTRACT (Continue on reverse if necessary and identify by block number)  Polypyrrole (Ppy) is one of the most extensively investigated of the electronically conductive polymers. Nevertheless, there is still much we don't understand about this interesting and useful material. One of the most persistent mysteries involves <u>simple chemical composition</u> . Doped PPy should have the empirical formula $C_4H_3NX_z$ where $X^-$ is the dopant counterion and $z$ is the fractional doping level; $z$ is typically on the order of 0.3. However, elemental analyses of PPy typically show empirical formulas like $C_4H_3NX_zO_y$ where $y$ ranges from 0.3 to 0.7 unaccounted for oxygen atoms per pyrrole ring. This paper presents IR spectral data which suggests that the oxygen in PPy is present as covalently-bound hydroxide. Analogous IR investigations of poly(N-methylpyrrole) films show that this polymer is also hydroxylated. The hydroxy substitution present in these polymers undoubtedly results from nucleophilic attack by water on the nascent polycationic chains.						
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS				21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert Nowak				22b. TELEPHONE (Include Area Code) (202) 696-4410		22c. OFFICE SYMBOL

**INFRARED INVESTIGATIONS OF PRISTINE POLYPYRROLE - IS THE POLYMER  
CALLED POLYPYRROLE REALLY POLY(PYRROLE-CO-HYDROXYPYRROLE)?**

Junting Lei and Charles R. Martin\*  
Department of Chemistry  
Colorado State University  
Fort Collins, CO 80523

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

\*Corresponding author.



92 5 06 007

**92-12339**  
■■■■■■■■■■

## ABSTRACT

Polypyrrole (PPy) is one of the most extensively investigated of the electronically conductive polymers. Nevertheless, there is still much we don't understand about this interesting and useful material. One of the most persistent mysteries involves *simple chemical composition*. Doped PPy should have the empirical formula  $C_4H_3NX_z$ , where  $X^-$  is the dopant counterion and  $z$  is the fractional doping level;  $z$  is typically on the order of 0.3. However, elemental analyses of PPy typically show empirical formulas like  $C_4H_3NX_2O_y$  where  $y$  ranges from 0.3 to 0.7 unaccounted for oxygen atoms per pyrrole ring. This paper presents IR spectral data which suggest that the oxygen in PPy is present as covalently-bound hydroxide. Analogous IR investigations of poly(N-methylpyrrole) films show that this polymer is also hydroxylated. The hydroxy substitution present in these polymers undoubtedly results from nucleophilic attack by water on the nascent polycationic chains.

Polypyrrole is one of the most extensively investigated of the electronically conductive polymers (1-10). Nevertheless, there is still much we don't understand about this polymer. One of the most persistent mysteries involves *simple chemical composition*. Doped polypyrrole should have the empirical formula  $C_4H_3NX_z$ , where  $X^-$  is the dopant counterion and  $z$  is the fractional doping level. However, elemental analyses of polypyrrole typically show empirical formulas like  $C_4H_3NX_zO_y$ , where  $y$  ranges from 0.3 to 0.7 unaccounted for oxygen atoms per pyrrole ring (2-5). While a number of explanations have been proposed (2-6), the chemical identity of this oxygen in polypyrrole is currently unknown.

Diaz et al. have, however, provided an interesting clue - this unaccounted for oxygen can be eliminated by electrochemically synthesizing the polymer in rigorously-dried acetonitrile (7,8). We have recently conducted infrared (IR) analyses on polypyrrole film synthesized in rigorously dried acetonitrile and in  $CH_3CN$  containing various amounts of water. These analyses suggest that the oxygen in polypyrrole is present as covalently-bound hydroxide. The results of these investigations are reported here.

The key to ascertaining the chemical identity of the O in polypyrrole was in obtaining reliable IR spectra for the undoped material. As recently pointed out by Zerbi, this has proved to be problematic because undoped polypyrrole is not air-stable (9,10). We have circumvented this problem by designing a novel spectroelectrochemical cell which allows for synthesis and IR and electrochemical characterization of thin polypyrrole films, while rigorously protecting these films from air (11). Polypyrrole films were synthesized galvanostatically onto an IR-transparent window in the cell (11). Polymerization solutions were 0.1 M in pyrrole and 0.1 M in  $LiClO_4$ . The solvent was either rigorously dried (11)

acetonitrile, as-received HPLC grade  $\text{CH}_3\text{CN}$  (this solvent contains trace, ca. 0.02 %, water), or HPLC grade  $\text{CH}_3\text{CN}$  to which was added 1 or 2 % water by volume.

The polypyrrole films synthesized from these various solvents are denoted as  $\text{PPy}_{\text{dry}}$ ,  $\text{PPy}_{0.02}$ ,  $\text{PPy}_{1.0}$ , and  $\text{PPy}_{2.0}$ . All films were ca. 400 nm thick (12). After synthesis, the polymerization solution was drained from the cell and the film was rinsed (in situ) with copious quantities of rigorously-dried  $\text{CH}_3\text{CN}$ . Excess solvent was then removed from the film by training a stream of purified (11) Ar onto the film. After drying, an IR spectrum for the doped material was obtained. The cell was then refilled with electrolyte and the film was electrochemically undoped at -0.8 V vs. SCE. The film was then rinsed and dried as before and an IR spectrum for the undoped material was obtained.

FTIR spectra for the *doped* forms of  $\text{PPy}_{\text{dry}}$ ,  $\text{PPy}_{0.02}$ ,  $\text{PPy}_{1.0}$ , and  $\text{PPy}_{2.0}$  were, within experimental error, identical. These spectra (e.g. Figure 1) show the featureless rise in absorbance with energy, at energies above  $1600\text{ cm}^{-1}$ , and a characteristic (9-11) series of seven absorption peaks at energies below  $1600\text{ cm}^{-1}$ . FTIR spectra for the *undoped* films (Figure 2) are quite different. Note, for example, the dramatic attenuation in absorbance at energies above  $1600\text{ cm}^{-1}$ ; this is expected because the absorbance in this region arises from the free charge carriers present in the doped material (5,9,13). The decreased absorbance of the undoped material allows some interesting spectral features to emerge. For example, spectra for the undoped films clearly show the N-H stretching mode at  $3400\text{ cm}^{-1}$ .

More importantly, the spectra for the undoped films synthesized in  $\text{CH}_3\text{CN}$  containing water show a sharp peak at  $3558\text{ cm}^{-1}$  that is not observed in  $\text{PPy}_{\text{dry}}$  (Figure 2). This peak is clearly due to an O-H stretching mode and its narrowness and position indicate that it does

not arise from water. That this O-H peak is not from water is also supported by the lack of a water bending peak at ca.  $1620\text{ cm}^{-1}$  (14). If the  $3558\text{ cm}^{-1}$  peak arises from covalently-bound -OH, we would expect to see a band in the region of  $1260$  to  $1000\text{ cm}^{-1}$  associated with the corresponding C-O vibration (15). In agreement with this prediction,  $\text{PPy}_{0.02}$ ,  $\text{PPy}_{1.0}$ , and  $\text{PPy}_{2.0}$  all show an intense band at  $1115\text{ cm}^{-1}$ ; this band is not observed in  $\text{PPy}_{\text{dry}}$ .

The identity of the  $3558\text{ cm}^{-1}$  band can also be ascertained via an isotope exchange experiment. A polypyrrole film was synthesized in  $\text{CH}_3\text{CN}$  solution containing 1 %  $\text{H}_2\text{O}$  and then reduced as before. The film was then exposed to  $\text{D}_2\text{O}$  by filling the cell with pure liquid  $\text{D}_2\text{O}$ . The film was then dried for six hours as described above. If the  $3558\text{ cm}^{-1}$  peak is due to O-H, exposure to  $\text{D}_2\text{O}$  should cause this band to disappear; furthermore, a new band, associated with the corresponding O-D vibration, should appear at ca.  $2640\text{ cm}^{-1}$  (14). Figure 3 shows the infrared spectrum for the  $\text{D}_2\text{O}$ -exposed film. In agreement with the above predictions, this film shows no trace of either the  $3558\text{ cm}^{-1}$  (O-H) or  $3400\text{ cm}^{-1}$  (N-H) bands and two new bands at  $2643\text{ cm}^{-1}$  (O-D) and  $2571\text{ cm}^{-1}$  (N-D) appear (Figure 3). This isotope exchange experiment strongly supports the proposition that covalently-bound -OH is present in these polypyrrole films.

A final point is worth making about the spectrum shown in Figure 3. Note that the increase in absorbance above  $1600\text{ cm}^{-1}$  indicates that exposure of the undoped polypyrrole film to  $\text{D}_2\text{O}$  causes the film to become partially doped. We have observed an analogous effect upon exposure of undoped polypyrrole films to  $\text{H}_2\text{O}$ . The nature of this water-induced doping process is currently unclear. We are investigating this phenomenon further.

The data obtained here indicate that the excess oxygen observed in most polypyrrole

samples is present as covalently-bound hydroxide. The investigations of Tsai et al. (16) provide an explanation for the genesis of this hydroxy substitution. As part of their investigations of substituted polythiophenes, Tsai et al. have suggested that water can undergo nucleophilic attack on the polycationic chain to yield the corresponding hydroxylated polymer (16). As in the studies described here, the water was present as a trace impurity in the acetonitrile used as the solvent for electrosynthesis (16). It seems likely that the same reaction is responsible for the hydroxy-substitution in polypyrrole.

If this is the case, other heterocyclic polymers should also be susceptible to this nucleophilic attack by water. To test this premise, we conducted analogous studies on poly(N-methylpyrrole) films. Figure 4 shows an FTIR spectrum for a poly(N-methylpyrrole) film synthesized in acetonitrile that contained 0.02 % water. The bands due to -OH are, indeed, observed and, again, these bands are not observed in films synthesized in rigorously-dried CH<sub>3</sub>CN. Thus, nucleophilic attack by water appears to be a general phenomenon in heterocyclic polymer.

Finally, it is interesting that these polymers exist in the enol form rather than tautomerizing to the ketone. (The lack of tautomerization is supported by the absence of a carbonyl absorption in the infrared spectrum at 1710 cm<sup>-1</sup>; we have shown that polypyrrole samples that are chemically-synthesized at very low rates in water show this carbonyl band (5)). That the polymer prefers to stay as the enol is, however, not too surprising because formation of the ketone would interrupt the conjugation along the polymer chain.



Acknowledgements. This work was supported by the Air Force Office of Scientific Research and the Office of Naval Research.

#### FIGURE CAPTIONS

Figure 1. IR spectrum for doped polypyrrole film. This spectra is from PPy<sub>1.0</sub>.

Figure 2. IR spectra for undoped polypyrrole films. (A) PPy<sub>dry</sub>, (B) PPy<sub>0.02</sub>, (C) PPy<sub>1.0</sub>, (D) PPy<sub>2.0</sub>. These spectra were arbitrarily positioned one above the other.

Hence, the ordinate is an arbitrary absorbance axis. However, as a calibration point, for each spectrum, the absorbance at 4,000 cm<sup>-1</sup> was (A) 0.32 AU, (B) 0.95 AU, (C) 1.1 AU. (D) 1.1 AU.

Figure 3. IR spectrum for undoped PPy<sub>1.0</sub> after exposure of the film to D<sub>2</sub>O.

Figure 4. IR spectrum for an undoped poly(N-methylpyrrole) film that had been synthesized in acetonitrile containing ca. 0.02% water.

## References

1. Skotheim, T. A. Ed., *Handbook of Conducting Polymer*, Dekker, New York, 1986, Vol. 1, Chaps. 3, 8.
2. Salmon, M.; Diaz, A. F.; Logan, A. J.; Krounbi, M.; Bargon, J. *Mol. Cryst. Liq. Cryst.* 1982, 83, 265.
3. Ribo, J. M.; Dicko, A.; Tura, J. M.; Bloor, D. *Polym.* 1991, 32, 728.
4. Neoh, K. G.; Kang, E. T.; Tan, T. C. *J. Appl. Polym. Sci.* 1989, 37, 2170 .
5. Lei, J. T.; Cai, Z.; Martin, C. R. *Synth. Met.* 1992, 46, 53..
6. Qian, R.; Qiu, J. *Polym. J.* 1987, 19, 157.
7. Kanazawa, K. K.; Diaz, A. F.; Geiss, R. H.; Gill, W. D.; Kwak, J. F.; Logan, J. A.; Rabolt, J. F.; Street, G. B. *J. Chem. Soc. Chem. Commun.* 1979, 854.
8. Kanazawa, K. K.; Diaz, A. F.; Gill, W. D.; Grant, P. M.; Street, G. B.; Gardini, G. P.; Kwak, J. F. *Synth. Met.* 1980, 1, 329.
9. Street, G. B.; Clarke, T. C.; Krounbi, M.; Kanazawa, K. K.; Lee, V.; Pfluger, P.; Scott, J. C.; Weiser, G. *Mol. Cryst. Liq. Cryst.* 1982, 83, 253.
10. Tian, B.; Zerbi, G. *J. Chem. Phys.* 1990, 92, 3892.
11. Lei, J. T.; Liang, W.; Martin, C. R. *Synth. Met.* accepted.
12. Diaz, A. F.; Castillo, J. I.; Logan, J. A.; Lee, W. J. *Electroanal. Chem.* 1981, 129, 115.
13. Cai, Z.; Lei, J. T.; Liang, W.; Menon, V.; Martin, C. R. *Chem. Materials*, 1991, 3, 960.
14. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, 1963, p. 83.

15. See R. M. Silverstein et al. ed. *Spectrometric Identification of Organic Compounds*, John Wiley & Sons Inc. Chap. 3, 5th Ed., 1991.
16. Tsai, E. W.; Basak, S.; Ruiz, J. P.; Reynolds, J. R.; Rajeshwar, K. *J. Electrochem. Soc.* 1989, 136, 3683.

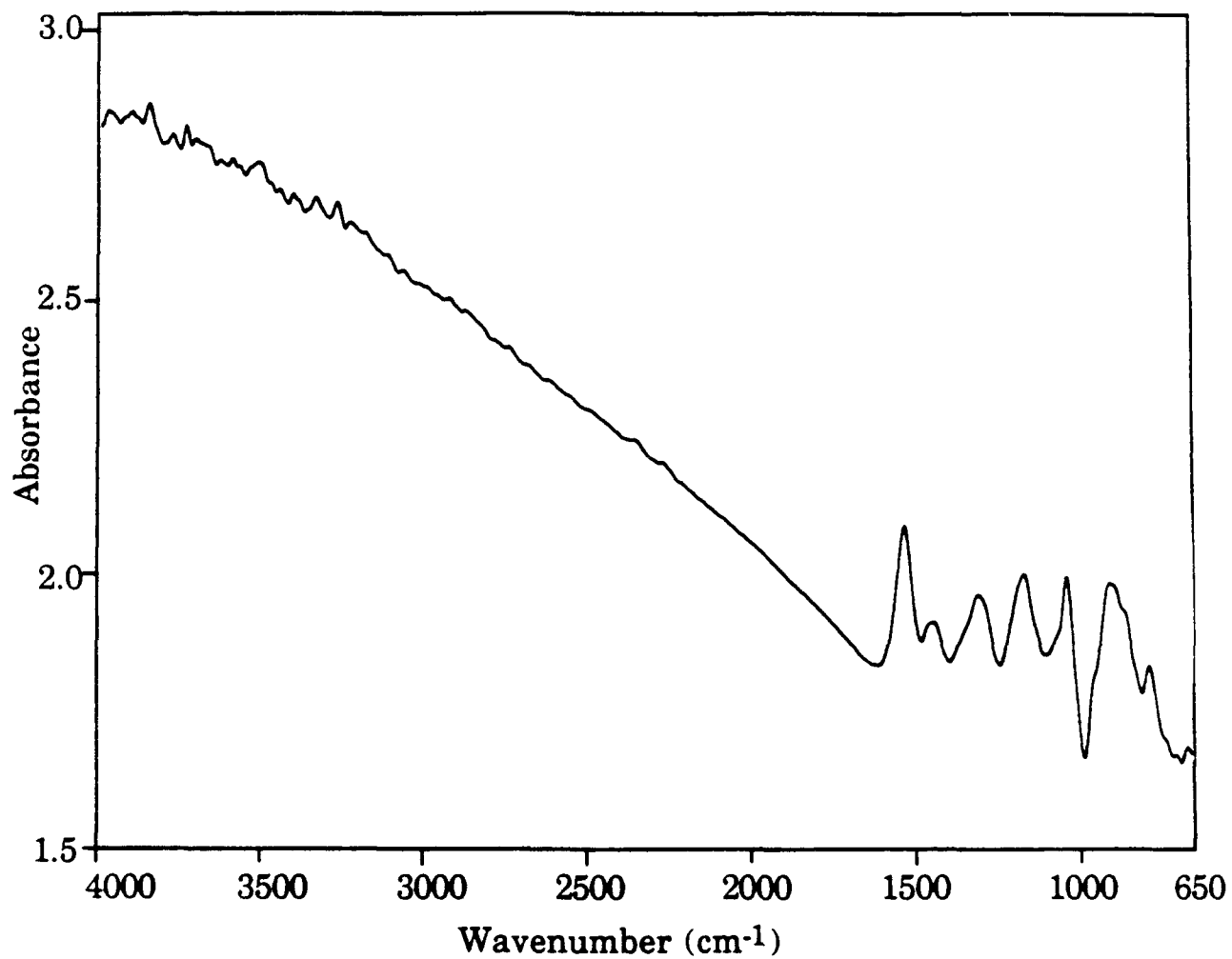


Fig. 1

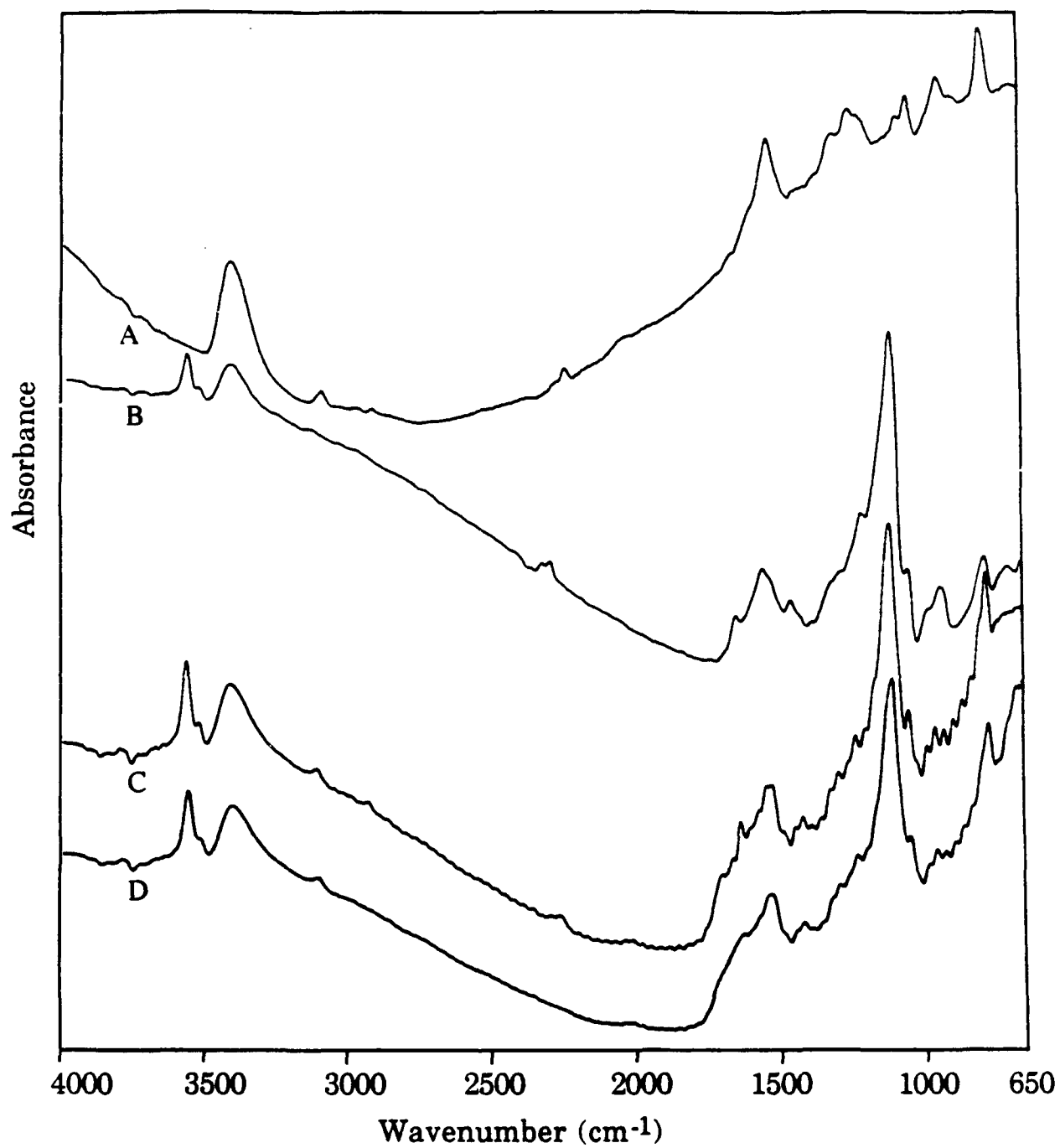


Fig. 2

