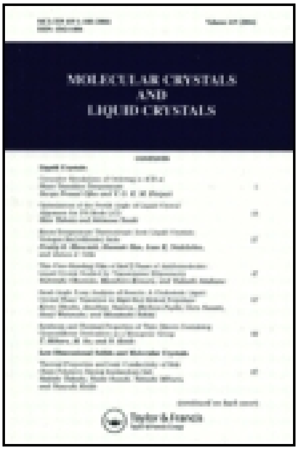

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Chemical modification of conducting polypyrrole films

M. Salmon [a], A. F. Diaz [a], A. J. Logan [a], M. Krounbi [a] & J. Bargon [a]

[a] IBM Research Laboratory, San Jose, California, 95193

To cite this article: M. Salmon, A. F. Diaz, A. J. Logan, M. Krounbi & J. Bargon (1982): Chemical modification of conducting polypyrrole films, Molecular Crystals and Liquid Crystals, 83:1, 265-276

To link to this article: http://dx.doi.org/10.1080/00268948208072175

Mol. Cryst. Liq. Cryst., 1982, Vol. 83, pp. 265–276
0026-8941/82/8301-0265$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

CHEMICAL MODIFICATION OF CONDUCTING POLYPYRROLE FILMS

M. SALMON, A. F. DIAZ, A. J. LOGAN,
M. KROUNBI, and J. BARGON
IBM Research Laboratory
San Jose, California 95193

Received for publication October 23, 1981

Conducting films of polypyrrole can be modified by introducing substitutents into the cationic pyrrole polymer or by varying the accompanying anion. The electrochemical route for the preparation of these films is particularly convenient for making these modifications since the variations are made in the selection of the monomer or the electrolyte. This eliminates the need for subsequent chemical treatments of the film. As expected, the electrochemical and conducting properties of the film are changed by these chemical modifications.

INTRODUCTION

A common characteristic of the electroactive redox films is that they are porous and incorporate high concentration of ions.[1-6] This is equally true for the films of highly conducting polymers such as polypyrrole,[7] polyacetylene,[8] poly-p-phenylene,[9] poly-p-phenylene vinylene,[10] and poly-p-phenylene sulfide.[11] In the case of the electrochemically oxidized polypyrrole films, the anion content remains in the range 0.25-0.33 anions per pyrrole ring for a wide variety of anions.[7a,b] In spite of this, the anion influences the oxidation-reduction kinetics of the polymer and produces a variation of 10^4 in the conductivity of the film.[7] In this regard, polypyrrole differs from polyacetylene, where both the level of oxidation and the conductivity can be different with each ion.[8] Thus, any attempts at modifying these films must consider the nature of the anion along with the use of substituents. The fact that the polypyrrole films are prepared electrochemically facilitates these modifications since the variations are made in the selection of the electrolyte or the monomer. We have now made a brief study of polypyrrole films modified by using different anions and by placing methyl substituents in the N- and β-position of the pyrrole ring. The results reveal that the selection of anions can be expanded to include sulfonate anions which are stable to the film preparation conditions and can improve the thermal stability of the films. As regards the methyl substituent, the properties of the film depends very much on the position of substitution.

EXPERIMENTAL

Films of polypyrrole were prepared in 99% aqueous acetonitrile as previously described.[7] Films of two different thicknesses were employed, thin films (200-1000Å thick) which were left attached to the electrode surface and were used for electrochemical analysis plus thick films (10-50μ thick) which were removed from the electrode and used for physical measurements. The thin films were prepared at constant potential on a 0.5 cm^2 platinum electrode and using 8 mC/cm^2. The concentration of all the electrolytes was 0.1M. Commercially available tetraethylammonium tetrafluoroborate, tetramethylammonium hexafluorophosphate, tetrabutylammonium hexafluoroarsenate, bisulfate, and perchlorate were dried at 90°C before use. Tetrabutylammonium fluorosulfonate, trifluoromethylsulfonate, p-toluenesulfonate, p-bromobenzenesulfonate, trifluoroacetate, nitrate, and fluoride were prepared by neutralization of the appropriate acid with tetrabutylammonium hydroxide in the usual manner.

The cyclic voltammetric analyses of pyrrole and the polypyrrole films were performed as previously described.[7c] The procedures for measuring the conductivities, flotation densities and scanning electron micrographs of the free-standing films are also described.[7c] The films used for these measurements and for the elemental analyses were prepared and washed as before.[7c] The temperature dependent conductivity study was performed using a four probe technique. The measurements were made in air with the films mounted on a sapphire disk placed on a heating element.

RESULTS AND DISCUSSION

Anion Variation

Electrochemical Behavior. The anion of the electrolyte produces changes in the cyclic voltammogram for the oxidation reaction of pyrrole and of polypyrrole. The pyrrole oxidation reaction is irreversible and fairly complicated. This reaction will not be discussed here in detail except to mention that the E_{pa} values for this reaction appear in the region between +1.0 and +1.3V (50 mV/s) with all of the anions listed in Tables 1 and 2. This is not surprising since the E_{pa} values for irreversible reaction are sensitive to the solution conditions.

The oxidation reaction of the polypyrrole polymer, on the other hand, is coulombically reversible but also complicated. This reaction is accompanied by structural movement of the polymer chains on the electrode surface and is dependent on the diffusion process of the ions in the film.[7c] The various anions produce more noticeable changes on the voltammogram of the polymer than on that of the monomer. Aside from the shift in the E_{pc} values and broadening of the peaks, the voltammogram of the polymer will show additional peaks in both the anodic and cathodic sweeps which certain anions. This is seen in Fig. 1 where a different voltammogram is produced with each electrolyte for the reaction of a polypyrrole film (ca. 200Å thick). The anions used in these experiments are more nucleophilic than the inorganic anions used previously (BF_4^-, ClO_4^-, PF_6^-, etc.).[7c] The nucleophilicity is not strong enough, however, for the anion to react chemically with the cationic polymer. This variation in the form of the voltammogram with anion was observed earlier and explained in terms of the generation of electrochemically discrete centers in the film.[7c] The i_{pa} values scale linearly with sweep rate in the range 10 to 100 mV/s in every case. The $i_{pa}/A\nu$ (mA·s/V·cm^2) values obtained with the various salts are in the range 1.6-3.8. The i_p-ν relationship is consistent with the reaction of a surface localized species. However, the kinetics of this reaction must be slow as previously observed[1-7] and gives rise to different E_{pa} and E_{pc} values plus unsymmetrical peaks in the voltammogram. These films undergo a color change during the reaction from light yellow (neutral polymer) to brown-black (oxidized polymer) as was previously observed with the inorganic anions.[7b]

The various sulfonate anions behave like the BF_4^-, ClO_4^-, PF_6^-, etc. anions in the switching reaction of the polymer. The different peak shapes suggest that the anion influences the kinetics of the redox reaction, but not the thermodynamics since the E_p values are not appreciably shifted. Therefore, the thermodynamics of the reaction must be controlled, primarily by the nature of the polypyrrole polymer even though the oxidized film strongly affiliates a significant amount of anion.

Free Standing Films. The composition of the free-standing films of oxidized polypyrrole are listed in Table 1. These films consist of ca. 70% polymer and 30% anion (by weight). The films are hydroscopic and lose 5-7% moisture when dried at 110°C. The excess oxygen in the films containing perchlorate, bisulfate, and toluenesulfonate anion, suggests that these films retain moisture even after these drying conditions to the extent of 0.24, 0.39, and 0.18 H_2O molecules/pyrrole ring, respectively. The elemental analysis of the films containing BF_4^- and AsF_6^- do not show good material balance where the missing weight may be due to the presence of oxygen in the structure as is observed with the chemically prepared films.[12] With the FSO_3^- anion, the resulting films have a high hydrogen content for reasons yet unknown. Not shown in the tables is the data for the film with NO_3^- anion which is conducting ($\sigma = 18(\Omega cm)^{-1}$) but give a low total in the elemental analysis (83%) suggesting that it is highly oxygenated. In this regard, these films resemble the chemically prepared films and may result from the fact that nitrate ion is a mild oxidant. For the majority of the anions, the mole ratio of anion to pyrrole ring (m) varies within 12% of 0.3 (Table 2) even though there are major differences between these anions, e.g., in terms of polarizability, basicity, size, etc. This ratio agrees with the electrochemical result[7c] and again suggests that the level of oxidation of the polymer in the film is determined by the chemical nature of the polymer and much less by the nature of the anion. These results differ from those obtained with polyacetylene where the degree of oxidation of the polymer can be varied by exposing it to different chemical oxidants (which also produces the necessary anion).[8]

The topology of the growing surface of the film is also influenced by the electrolyte. Shown in Fig. 2 are the scanning electron micrographs of some of the films. Not all of the surfaces are shown since there are some similarities among them. For example, the films containing BF_4^-, AsF_6^-, NO_3^-, F^-, $CH_3C_6H_4SO_4^-$, and $BrC_6H_4SO_3^-$ have surfaces which resemble the films with CF_3COO^- and with FSO_3^-. The wide variation in the topologies of the surfaces again emphasize the complexity of the electropolymerization process which, among other things, produces regions in the films with different grow rates. The differences observed in the surface toplogies are not reflected in the packing structure of the bulk material since the flotation densities of the films show little variation. The density values listed in Table 2 are the average of four or five determinations and have a deviation of ±0.02 units.

The room temperature electrical conductivity (σ_0) is the other property of the film which is affected by the nature of the anion. As seen in Table 2, a variation of 10^4 can be produced in the conductivity of the films by the choice of the appropriate sulfonate anion. Thus, the nature of the anion seems important for those properties of the film which involve charge transport; i.e., redox reaction of the film and electrical conductivity. Ion diffusion is the limiting factor in the former process, while the role of the anion in the electron transport property of the oxidized film is unclear but may be related to the polarizability and the rotational/vibrational dynamics of the anion.

The conductivities are temperature dependent as shown in Fig. 3 where σ/σ_0, the ratio of the conductivity (in air) at temperature T (σ) to the room temperature conductivity, (σ_0) is plotted against temperature. The films which have conductivities in the range 50-100 $\Omega^{-1}cm^{-1}$ show only a small conductivity dependence on temperature and they decompose irreversibly at ca. 150°C as was previously shown for the BF_4^- films.[13] The less conducting films containing CF_3COO^- (12 $\Omega^{-1}cm^{-1}$) and $C_7H_7SO_3^-$ (4 $\Omega^{-1}cm^{-1}$) have a higher conductivity dependence on temperature and are more stable to heating. The σ/σ_0 versus temperature plot for these films are reproduced in the subsequent heating cycles in the temperature region below the maximum. The polypyrrole toluenesulfonate film (4 $\Omega^{-1}cm^{-1}$) has the highest temperature stability of the films considered and it decomposes at 280°C. The conductivities of these films were not measured at temperatures below room temperature, although our previous work shows that the conductivity of polypyrrole tetrafluoroborate decreases by a factor of 3-4 when the film is cooled to liquid nitrogen temperature.[7c]

Methyl Substituent

The methyl substituent produces major changes on the properties of the polypyrrole BF_4 films. With the methyl group on the N-position of the pyrrole ring, the neutral film is less easily oxidized and thus less sensitive to oxygen compared to polypyrrole, i.e., the E° of poly-N-methylpyrrole (0.5V) is shifted anodically by 0.65V but the degree oxidation is effectively unchanged, 0.23-0.29 charges/pyrrole ring. The peaks in the cyclic voltammogram are broader than for polypyrrole indicating slower redox kinetics. The room temperature conductivity ($10^{-3}(\Omega cm)^{-1}$) is five orders of magnitude less than polypyrrole, even though the general appearance and flotation density (1.46 gcm^{-3}) is like the polpyrrole film.

With the methyl group in the β position, the film is more easily oxidized than the above. The cyclic voltammogram for poly-β-methylpyrrole shows peaks at -250 mV (E_{pa}) and -300 mV (E_{pc}) which are ca. 100 mV less anodic than the peaks for polypyrrole. The degree of oxidation is as above. These films have a room temperature conductivity of 4 Ωcm^{-1} and a flotation density of 1.36 gcm^{-3}. Although less dense, the general appearance of the films is like polypyrrole. As regards to the structure of this polymer, it is probably an α,α'-coupled linear chain like polypyrrole, however, less regular because adjacent pyrrole rings along the chain may have β-methyl/β-methyl or β-methyl/β-hydrogen arrangements.

In summary, our results suggest that more emphasis should be placed on the nature of the anion affiliated with these oxidized polymers. Because the anion produces changes in the redox and electron transport properties of the films, it becomes a practical alternative - to modifying the properties of the films. This is particularly true since the electrochemical approach to preparing these conducting films permits us to expand the number of anions under consideration and to include sulfonate anions. Variation of the anion in combination with chemical derivatization of the polymer structure may prove important for designing polymers with the desired properties.

ACKNOWLEDGMENTS

The authors wish to thank Mr. B. S. Hall for his technical assistance in certain aspects of this work.

TABLE 1

Atom Mole Ratios from Elemental Analyses of Various Polypyrrole Films

Anion	Pyrrole Ring[a]			Anion[a]	Material Balance	Oxygen Eq. of Missing Wt
	C	H	N			
BF_4^-	(4.0)	3.63	0.93	B 0.22, F 0.97, O 0.36	97.0	
PF_6^-	(4.0)	3.53	1.0	P 0.25, F 1.35	100.0	--
AsF_6^-	(4.0)	3.15	1.0	As 0.315, F 1.6	94.59	0.34
ClO_4^-	(4.0)	3.53	1.0	Cl 0.36, O 1.62	96.15	
HSO_4^-	(4.0)	4.16	0.89	S 0.28, O 1.12[b]	96.14	0.39
FSO_3^-	(4.0)	6.0	0.98	F 0.39, S 0.36, O 0.89[b]	100.0	--
$CF_3SO_3^-$	4.0	3.39	(1.0)	C 0.72, F 1.01 S 0.33, O 1.07[b]	100.0	--
$BrC_6H_4SO_3^-$	4.0	3.05	(1.0)	C 1.97, H 1.32, Br 0.34 S 0.33, O 0.96[b]	100.0	--
$C_7H_7SO_3^-$	4.0	3.60	(1.0)	C 2.51, H 2.51, S 0.32, O 0.96[b]	97.71	0.18
CF_3COO^-	4.0	2.76	(1.0)	C 0.46, F 0.85, O 0.54[b]	100.0	--

[a] Values are normalized to the value in parentheses.
[b] Oxygen value by difference.

TABLE 2

Summary of Data for Various Polypyrrole Films[14]

Anion	m	d/gcm^{-3}	$\sigma_{25°}(\Omega cm)^{-1}$
BF_4^-, PF_6^-, AsF_6^-	0.25-0.32	1.48	30-100
ClO_4^-	0.30	1.51	60-200
HSO_4^-	0.30	1.58	0.3
FSO_3^-	--	1.47	10^{-2}
$CF_3SO_3^-$	0.31	1.48	0.3-1
$BrC_6H_4SO_3^-$	0.33	1.58	50
$CH_3C_6H_4SO_3^-$	0.32	1.37	20-100
CF_3COO^-	0.25	1.45	12

REFERENCES

1. (a) L. L. Miller and M. R. Van de Mark, J. Electroanal. Chem. 88, 437 (1978); (b) ibid., J. Amer. Chem. Soc. 102, 338 (1980) and references therein.
2. (a) A. Merz and A. J. Bard, J. Amer. Chem. Soc. 100, 3222 (1978); (b) K. Itaya and A. J. Bard, Anal. Chem. 50, 1487 (1978).
3. (a) N. Oyama and F. C. Anson, J. Amer. Chem. Soc. 101, 739, 3450 (1979); (b) ibid., J. Electrochem. Soc. 127, 247, 248 (1980).
4. (a) F. B. Kaufman and E. M. Engler, J. Amer. Chem. Soc. 101, 547 (1979); (b) F. B. Kaufman, A. H. Schroeder, E. M. Engler, and V. V. Patel, Appl. Phys. Lett. 36, 422 (1980) and references therein.
5. (a) J. R. Lenhard and R. W. Murray, J. Amer. Chem. Soc. 100, 7870 (1978); (b) R. J. Nowak, F. A. Schultz, M. Umeña, R. Lam, and R. W. Murray, Anal. Chem. 52, 315 (1980).

6. M. F. Dautartas and J. F. Evans, J. Electroanal. Chem. 109, 301 (1980).
7. (a) A. F. Diaz, K. K. Kanazawa, and G. P. Gardini, J. Chem. Soc., Chem. Comm., 635 (1979); (b) A. Diaz, Proceedings to be International Conference on Low-Dimensional Synthetic Metals, Chemica Scripta, 1981; (c) A. F. Diaz, J. I. Castillo, J. A. Logan, and W. Y. Lee, J. Electroanal. Chem., 0000 1981.
8. S. C. Gau, J. Mulliken, A. Pron, A. G. MacDiarmid, and A. J. Heeger, J. Chem. Soc., Chem. Comm., 662 (1979).
9. D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, and R. H. Baughman, J. Chem. Phys. 71, 1506 (1979).
10. G. E. Wnek, J. C. W. Chien, F. E. Karasz, and C. P. Lillya, Polymer 20, 1441 (1979).
11. J. F. Raybolt, T. C. Clarke, J. R. Reynolds, and G. B. Street, J. Chem. Soc., Chem. Comm., 347 (1980).
12. (a) L. Chierici and G. P. Gardini, Tetrahedron 22, 53 (1966); (b) V. Bocchi, L. Chierici, and G. P. Gardini 23, 737 (1967); (c) V. Bocchi, L. Chierici, G. P. Gardini, and R. Mondelli, Tetrahedron 26, 4073 (1970).
13. K. K. Kanazawa, A. F. Diaz, M. T. Krounbi, and G. B. Street, J. Syn. Metals, 0000 (1982).
14. A. Diaz and K. Kanazawa, Comprehensive Reviews, J. S. Miller, Ed., Plenum Press, in press.

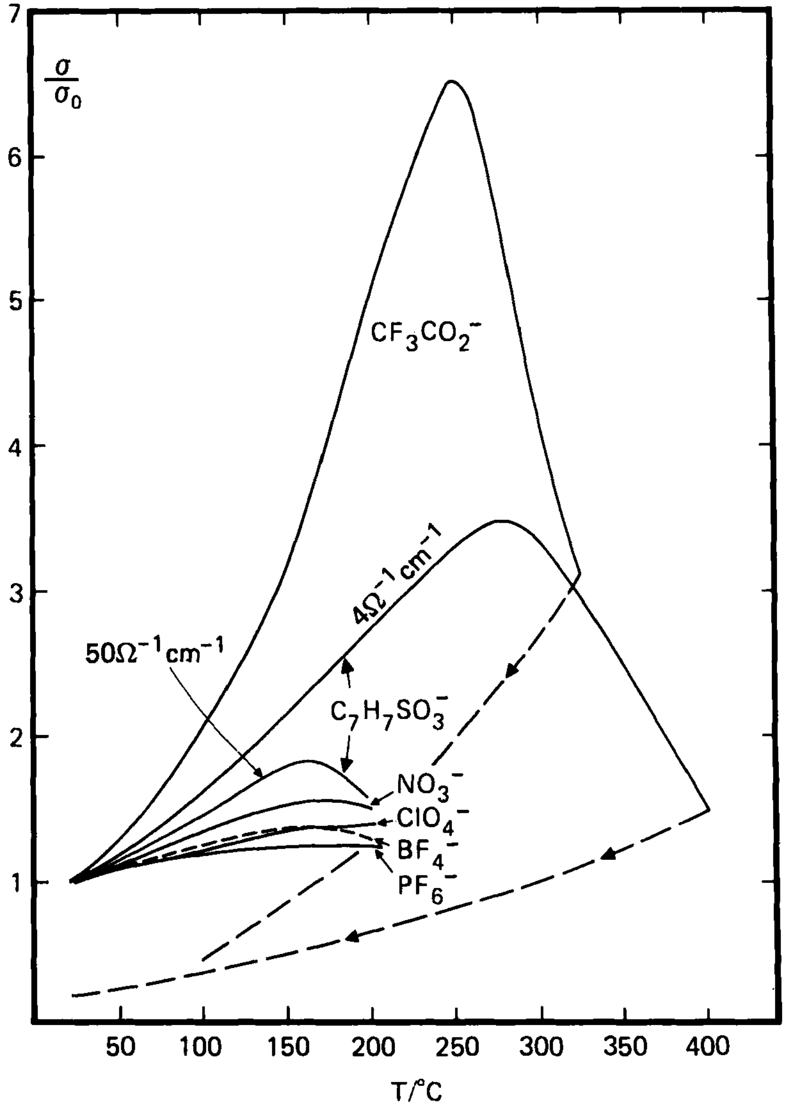

FIGURE 1 Cyclic voltammograms of polypyrrole films on platinum in acetonitrile containig 0.1M electrolyte.

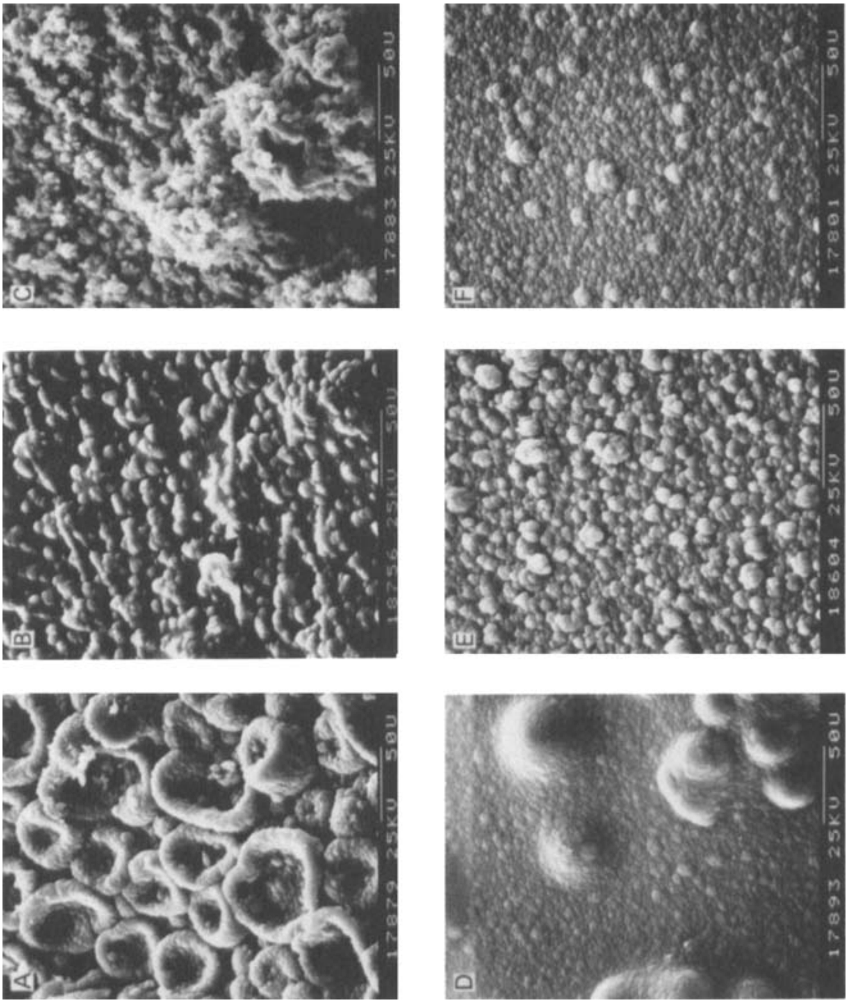

FIGURE 2 Scanning electron micrographs of polypyrrole film surfaces. The anion in the film is (A) hexafluorophosphate, (B) perchlorate, (C) sulfate, (D) fluorosulfonate, (E) trifluoromethylsulfate, and (F) trifluoroacetate.

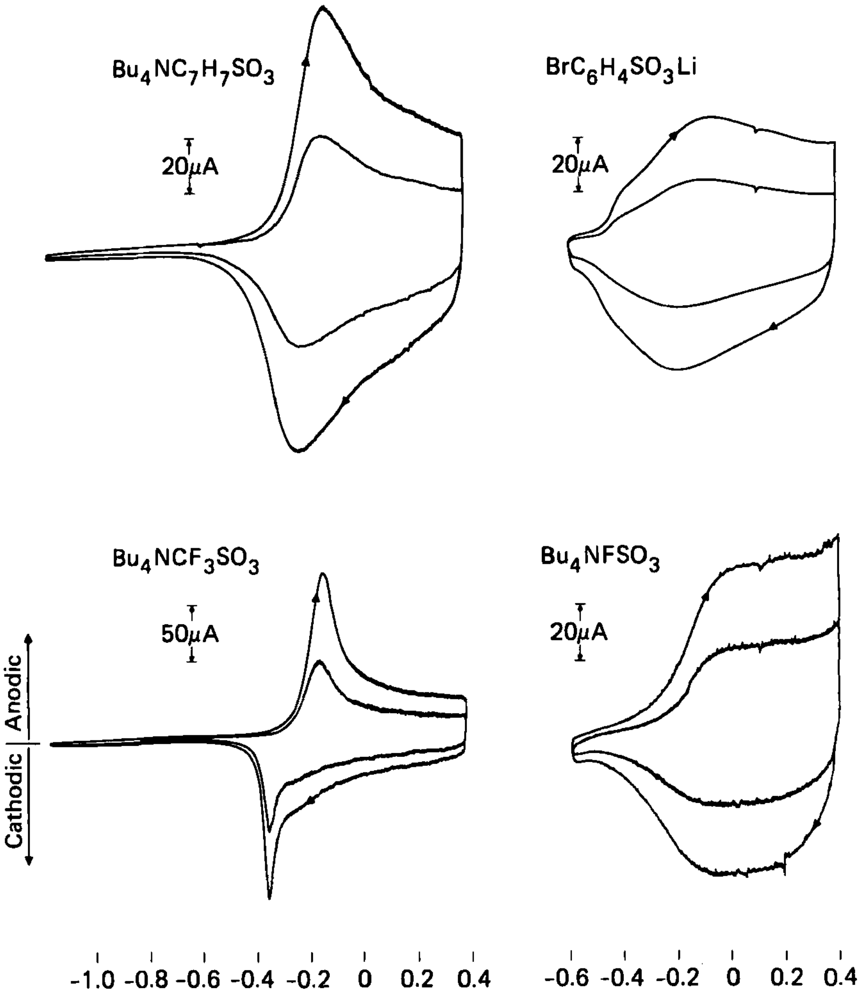

FIGURE 3 Plot of σ/σ_0 versus temperature for several conducting polypyrrole films.