

AD-A189 575

VAPOR ABSORPTION AND CONDUCTIVITY IN POLY(ETHYLENE
OXIDE)-SALT-PROPYLENE (U) ROCKWELL INTERNATIONAL
ANAHEIM CA SCIENCE CENTER M M NICHOLSON ET AL NOV 87

1/1

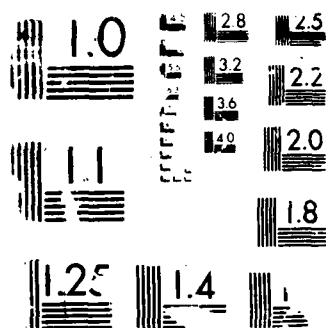
UNCLASSIFIED

SC5384 TR N00014-77-C-0636

F/G 7/3

ML





RESOLUTION TEST CHART

AD-A189 575

OFFICE OF NAVAL RESEARCH

Contract N00014-77-C-0636

R&T Code 413d004

Technical Report No. 8

Vapor Absorption and Conductivity in
Poly(ethylene Oxide)-Salt-Propylene Glycol Films

by

M. M. Nicholson and F. A. Pizzarello

Prepared for Publication

in the

Journal of the Electrochemical Society

Science Center
Rockwell International Corporation
Anaheim, CA

November 1987

Reproduction in whole or in 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.

DTIC FILE COPY

DTIC
ELECTE
JAN 05 1988
S D H

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

AD-A189573-

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT This document has been approved for public release and sale; its distribution is unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) SC5384.TR			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Rockwell International Science Center		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c. ADDRESS (City, State and ZIP Code) P.O. Box 3105 Anaheim, CA 92803			7b. ADDRESS (City, State and ZIP Code) 800 North Quincy Arlington, VA 22217		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State and ZIP Code) Vapor Absorption and Conductivity in Poly(ethylene Oxide)-Salt-Propylene Glycol Films			10. SOURCE OF FUNDING NOS.		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO. R&T Code 413d004
11. TITLE (Include Security Classification) Glycol Films					
12. PERSONAL AUTHOR(S) M. M. Nicholson and F. A. Pizzarello					
13a. TYPE OF REPORT Technical No. 8		13b. TIME COVERED FROM 1/1/85 TO 8/31/87	14. DATE OF REPORT (Yr., Mo., Day) November 1987		15. PAGE COUNT 23
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GR	Poly(ethylene oxide), propylene glycol, solid polymer electrolytes, conductivity		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
The use of propylene glycol (PG) as a plasticizer to increase the conductivities of solid poly(ethylene oxide) (PEO)-salt electrolyte films was investigated. The film conductances were measured at various times during exposure to PG vapor while the absorbed PG was monitored by IR spectroscopy. Spontaneous loss of PG following absorption was observed with PEO-LiBF₄-PG films but not when the salt was LiCl, KCl, or a combination of LiBF₄ and KCl. With the composition (PEO)_{4.1}LiBF₄(KCl)_{0.70}, a conductivity of 4x10⁻⁵ ohm⁻¹cm⁻¹ at 23°C was attained.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Robert J. Nowak			22b. TELEPHONE NUMBER (Include Area Code) (202) 696-4409	22c. OFFICE SYMBOL ONR-Code 1113	

VAPOR ABSORPTION AND CONDUCTIVITY IN POLY(ETHYLENE OXIDE)-
SALT-PROPYLENE GLYCOL FILMS

M. M. Nicholson

Rockwell International Science Center, Anaheim, California 92803

F. A. Pizzarello

Rockwell International Corporation, Autonetics Electronics
Systems Division, Anaheim, California 92803

ABSTRACT

The use of propylene glycol (PG) as a plasticizer to increase the conductivities of solid poly(ethylene oxide) (PEO)-salt electrolyte films was investigated. The film conductances were measured at various times during exposure to PG vapor while the absorbed PG was monitored by IR spectroscopy. Spontaneous loss of PG following absorption was observed with PEO-LiBF₄-PG films but not when the salt was LiCl, KCl, or a combination of LiBF₄ and KCl. With the composition (PEO)_{4.1}LiBF₄(KCl)_{0.70}, a conductivity of $4 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 23°C was attained.

For
FI
ed
tionBy
Distribution/
Availability Code
Avail and/or
Special

Dist





The desire for solid-state lithium batteries has motivated extensive research on organic polymer electrolytes during the last ten years. With the battery application foreseen, attention has been focused on aprotic systems, and, for low-rate cells, conductivities as low as $10^{-5} \text{ohm}^{-1} \text{cm}^{-1}$ have been of practical interest. Notable progress in this field has been made by using complexes of simple salts with aliphatic polyethers such as poly(ethylene oxide) (PEO)⁽¹⁾ and with certain polyphosphazenes.⁽²⁾ Solid electrolytes are also of major interest to potential users of electrochromic displays and other electrochemical devices, but higher conductivity is preferred for fast response, and the absence of protons is not a general requirement.

It is now widely recognized that ion transport in the better polymer-salt electrolytes occurs primarily in amorphous regions; hence, a low crystal-to-glass transition temperature is a most desirable characteristic. Pursuing this concept further, some investigators have improved conductivities in polymer-salt systems by introducing a solvent component, or plasticizer.⁽³⁻⁵⁾ Shriver and co-workers used poly(ethylene glycol) (MW 300) to enhance the conductivities of polymer-salt complexes⁽³⁾ and of polymeric ionomers having only one mobile species.⁽⁴⁾ Reed, Geng, and Murray observed improved voltammetric behavior of electroactive solutes in solid PEO-LiCF₃SO₃ when acetonitrile vapor was present.⁽⁵⁾



Ultimately, a plasticized system may absorb enough solvent to reach a highly swollen gel condition. If ions are present, their mobilities can then approach those in the liquid plasticizer, with the polymer acting as an inert matrix rather than a conduction medium. Experimentally, the demarcation between the plasticized polymer and the incipient gel may not always be apparent. Either condition usually is acceptable from a device standpoint if it provides adequate conductivity, solid or semisolid handling characteristics, and thermal stability over the required operating and storage temperature ranges.

The absorption of water and its influence on ionic conduction in PEO-LiBF₄ films were investigated previously in this laboratory.⁽⁶⁾ Although conductivities as high as $3 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$ were attained, water in excess of the composition LiBF₄·3H₂O proved to be unstably absorbed. Under constant vapor pressure, much of the excess water escaped spontaneously from the film within a few minutes after its absorption, and a corresponding drop in conductivity to $\sim 2 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$ occurred.

The present paper reports on an effort to produce a more stable plasticized or gelled electrolyte with PEO and a low-volatility organic additive. Preferred characteristics of the



plasticizer included a high dielectric constant to promote ionic conduction and a wide liquid temperature range to reduce the tendency for evaporation or for phase separation on cooling. Graham *et al.* had observed extensive swelling of a PEO-type polymer, without syneresis, by propylene glycol (PG) and several other organic liquids.⁽⁷⁾ In that study, water fell within another group of solvents that also caused swelling initially but underwent syneresis, or spontaneous separation of liquid, on standing. The polymer in that investigation was prepared by crosslinking poly(ethylene glycol) of average molecular weight near 6,000 in the presence of 2-ethyl-2-hydroxymethylpropane-1,3-diol. In addition to its favorable swelling effect on the crosslinked polymer, PG has a relatively high dielectric constant of 32 at 20°C and a very wide liquid temperature range (f.p. -60°C; b.p. 188°C).⁽⁸⁾

With that background, we selected PG for investigation as a plasticizer of polymer-salt films prepared from high molecular-weight (MW 4,000,000) linear PEO. The use of thin films rather than bulk polymer specimens permitted much faster acquisition of data. The salts included KCl, which does not complex with PEO in the solvent-free condition, and LiCl and LiBF₄, which are known to form definite PEO complexes.⁽¹⁾ The uptake of PG from the vapor phase was monitored by recording the near-IR absorbance as a function of time, and the film resistance was measured at intervals in the same experiment. Although major swelling and exceptional conductivity were not found, the data



revealed some interesting contrasts in polymer electrolyte behavior with single and mixed salt components.

EXPERIMENTAL

The PEO, average MW 4,000,000, was from Polysciences, Inc.; the propylene glycol (1,3-propanediol) was a J. T. Baker product (b.p. 186-189°C), and the lithium fluoroborate was from Ozark-Mahoning. The other chemicals were reagent grade.

Casting solutions were prepared by dissolving the PEO and salt in boiling water and stirring until a uniform mixture was obtained. A typical solution contained 0.04 g PEO per gram of water. After cooling to room temperature, the liquid solution was manually cast onto a 2.54-cm diameter single-crystal sapphire disk bearing two parallel metal-strip electrodes, 1.27 cm wide and 0.06 cm long, and separated by 0.318 cm. The electrodes, consisting of sputtered gold electroplated with silver, were located off-center on the disk to provide an unobstructed region of the film on which an infrared spectrum could be recorded.

The film sample was predried under a blanketing stream of nitrogen and then placed, with a blank sapphire disk, in a double infrared (IR) cell which had four sapphire windows and a gas inlet and outlet.⁽⁶⁾ The cell was mounted in a Beckman DK-



2A spectrophotometer for in situ determination of conductance and IR absorbance. The measurements were made at room temperature, near 23°C, unless otherwise noted.

After final drying of the film by nitrogen, the gas stream was diverted through a container of PG, thereby introducing the glycol to the electrolyte through the vapor phase. Although the vapor pressure of PG is only 0.11 torr at 23°C, the uptake of glycol was evident almost immediately in the IR absorbance and increased conductance of the film.

Infrared spectra that included the OH band near 3 μm were recorded at times from about 5 to 450 min following admission of the glycol. The absorbance at 3.05 μm was taken as a measure of the glycol content of the film. Calibration at this wavelength relative to pure liquid glycol was done by obtaining spectra on weighed glycol films approximately 4 μm thick, held by surface tension between two of the polished sapphire disks. An absorbance of 1.00 unit corresponded to 0.336 mg/cm^2 of liquid PG.

Film conductances were measured at 1,000 hz. Most of the data were obtained by an ac current method in which the film sample with metal electrodes was connected in series with a variable sine-wave voltage source and an oscilloscope that had 1 megohm input resistance. Since the impedance was nearly



all resistive, the total resistance of the sample plus 1 megohm was found simply from the ratio of the peak-to-peak voltage output of the source to the peak-to-peak current measured on the oscilloscope. Resistances up to 10^9 ohms were determined in this way. At a later stage, when a Genrad 1689M Digibridge impedance meter became available, that instrument was used to verify the ac current method and to characterize several of the electrolyte films. Data from the impedance meter at 1,000 hz are reported in terms of the resistance in a parallel resistance-capacitance equivalent of the film sample.

Film thicknesses in the dry state were estimated two ways: (a) By use of a measuring microscope, with limited exposure of the film to air, and (b) by calculation from the lithium content of the film, assuming the dry film density to be 1.2 g/cm^3 (6). Lithium was determined by atomic absorption on a solution prepared by dissolving a known area of film in water after completion of the measurements. The dry-film thicknesses ranged from 29 to 81 μm .

RESULTS AND DISCUSSION

Table 1 gives the film compositions and thicknesses and summarizes results of the conductance measurements. Total absorbances and resistances of films containing the various salts are plotted as functions of time in Fig. 1-4.



That absorbance (A_t) includes the loss of light due to the glycol plus any residual loss due to scattering.

Absorption of PG. For KCl and LiCl films, the absorption process appeared to be essentially normal, with gradual uptake of PG on exposure of the film to the glycol vapor. However, the data did not fit a simple diffusion model. Adapting the treatment of Anderson and Saddington for diffusion in a slab of finite thickness,⁽⁹⁾ one would expect, at long times, a linear increase of absorbance with time. Such plots (not shown) for the films containing KCl or LiCl were nonlinear.

The behavior of the LiBF_4 preparations was more complex, as Fig. 3 indicates. In that case, the glycol content of the film reached a maximum at 1 hr and then gradually decreased toward a constant level. This spontaneous loss occurred under constant partial pressure of PG in the gas phase. It closely resembles the loss of water from films of $\text{PEO-LiBF}_4\text{-H}_2\text{O}$ or salt-free $\text{PEO-H}_2\text{O}$ reported previously.⁽⁶⁾ Such losses apparently are caused by increased ordering of the polymer. Surprisingly, the loss was not observed in PEO films containing both LiBF_4 and KCl. Fig. 4 represents such a case. The curve for absorbance vs time shows an inflection near 50 min and then continually rises to approach a constant value. It is not yet clear what initiates restructuring of the polymer or why this was not observed when KCl or LiCl was present as a major component of the film.



The PEO-salt films in the present study actually underwent very little swelling. For example, Film 8 at 120 min contained only 0.10 g PG per gram of PEO, based on the IR absorbance calibration with liquid PG. In contrast, the crosslinked PEO gel of Graham *et al.* absorbed as much as 4.5 times its own weight of PG.⁽⁷⁾ This major difference in affinity for PG could be due to steric differences in the polymers or to the presence of hydrogen-bonding OH groups in the gel of the crosslinked polymer.

Conductance. The measured film resistance ranged from 1×10^9 ohms in solvent-free PEO-salt preparations to 1.2×10^6 ohms in Film 8, which contained both LiBF_4 and KCl , after a 2-hr exposure to PG vapor. When the sample geometry is taken into account, the latter resistance corresponds to a bulk conductivity of approximately $4.0 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$.

The conduction behavior depended on the type of salt present. This is evident in Fig. 5-7, where the measured conductances ($1/R$) are plotted as functions of $(A_t - A_0)$. A_t is the absorbance at $3.05 \mu\text{m}$ at time t and A_0 is the initial absorbance, or apparent absorbance, before introduction of the glycol. With KCl , the conductance was low and not highly dependent on the PG concentration. That behavior could result if all of the salt dissolved at an early stage and only a



moderate decrease in ion pairing or increase in mobility occurred on dilution. The LiCl films showed a stronger dependence of conductance on the PG content, which could be represented by three linear segments on the log-log plots in Fig. 5. At this stage, it would be speculative to associate all of these changes in slope with specific mechanisms. However, the steepest rises observed with LiCl (Film 2) and LiCl + KCl (Film 7) may have signified a flooded condition in which the polymer layer was essentially shorted by a liquid electrolyte phase.

The spontaneous loss of PG from PEO-LiBF₄-PG films is manifested in peculiar shapes of the conductance-absorbance plots in Fig. 6. Within the times of the experiments, this system clearly was in a different regime from those of the KCl, LiCl, or combined LiBF₄-KCl preparations. With LiBF₄ only, the conductivity stabilized, after several hours, at 0.2 to 1×10^{-5} ohm⁻¹cm⁻¹, depending on the film sample.

Film 8, Fig. 7, attained the highest conductivity observed, 4.0×10^{-5} ohm⁻¹cm⁻¹ without PG loss or a drastic increase in the slope of $(1/R) \text{ vs } (A_t - A_0)$. This conductivity would be adequate for an electrochromic display cell if the electrolyte layer thickness did not exceed 10 μm ; it is within a useful range, but is not outstanding, for such a high-rate device. It may be compared with the value of 2.7×10^{-5} ohm⁻¹cm⁻¹ at 30°C reported



by Shriver and co-workers for a solid complex of LiCF_3SO_3 and a methoxyethoxyethoxide phosphazene polymer (MEEP), without a plasticizer.⁽²⁾

CONCLUSIONS

High-molecular-weight PEO-salt films plastized with a small proportion of PG attained a room temperature conductivity of at least $4 \times 10^{-5} \text{ ohm}^{-1}\text{cm}^{-1}$.

The PG uptake in these systems was much less than the PG uptake reported in the literature for PEO crosslinked in the presence of 2-ethyl-2-hydroxymethylpropane-1,3-diol.

The complication of spontaneous PG loss occurred in PEO- LiBF_4 -PG films, but the loss was prevented or inhibited if the film contained KCl in addition to LiBF_4 . Films in the PEO-KCl-PG or PEO- LiCl -PG systems did not lose PG spontaneously under the conditions of this investigation.

**ACKNOWLEDGMENT**

This work was supported in part by the Office of Naval Research. The lithium analyses were provided by H. D. Kammeyer of Rockwell's Material and Processes Laboratory at Anaheim.



REFERENCES

1. M. B. Armand, J. M. Chabagno, and M. J. Duclot, p. 131 in P. Vashista, J. N. Mundy, and G. K. Shenoy, eds., "Fast Ion Transport in Solids," Elsevier North Holland, 1978.
2. P. M. Blonsky, D. F. Shriver, P. Austin, and H. R. Allcock, Solid State Ionics, 18-19, 258 (1986).
3. R. Spindler and D. F. Shriver, Macromolecules, 19, 347 (1986).
4. L. C. Hardy and D. F. Shriver, J. Am. Chem. Soc., 107, 3823 (1985).
5. R. A. Reed, L. Geng, and R. W. Murray, J. Electroanal. Chem., 208, 185 (1986).
6. M. M. Nicholson and T. P. Weismuller, J. Electrochem. Soc., 132, 89 (1985).
7. W. B. Graham, N. E. Nwachuku, and D. J. Walsh, Polymer, 23, 1345 (1982).
8. G. J. Janz and R. P. T. Tomkins, "Nonaqueous Electrolytes Handbook," Vol. 1, Academic Press, New York, 1972.
9. J. S. Anderson and K. Saddington, J. Chem. Soc., S381 (1949).

TABLE 1. CHARACTERISTICS OF PEO-SALT-PG FILMS

FILM	COMPOSITION ^a	DRY THICKNESS		SELECTED DATA		
		MICROSC (μm)	Li ANAL (μm)	TIME ^b (MIN)	CONDITION ^c	MOLE RATIO ^d PG/Li
1	(PEO) _{5.4} KCl	-	-	114	HIGHEST MEAS CONDUCTANCE	-
2	(PEO) _{3.6} LiCl	-	-	33 75	1ST CHANGE OF SLOPE 2ND CHANGE OF SLOPE	-
3	(PEO) _{3.6} LiCl	-	-	20 45	1ST CHANGE OF SLOPE 2ND CHANGE OF SLOPE	-
4	(PEO) _{3.8} LiBF ₄	-	39	106 348	MAX ABSORBANCE FINAL ABSORBANCE	0.048 0.044
5	(PEO) _{3.8} LiBF ₄	-	29	89 240	MAX ABSORBANCE FINAL ABSORBANCE	0.30 0.25
6	(PEO) _{4.1} LiBF ₄	51	81	80 450	MAX ABSORBANCE FINAL ABSORBANCE	0.057 0.023
7	(PEO) _{4.1} LiBF ₄ (KCl) _{0.70}	38	40	10 30	1ST CHANGE OF SLOPE 2ND CHANGE OF SLOPE	0.093 0.34
8	(PEO) _{4.1} LiBF ₄ (KCl) _{0.70}	41	51	35 120	1ST (ONLY) CHANGE OF SLOPE HIGHEST MEAS CONDUCTANCE	0.054 0.34

CONDUCTIVITY^e
(OHM⁻¹CM⁻¹) $\times 10^6$ ~ 0.4
~ 0.5
~ 1
~ 1
~ 2
1.9^f
2.2^f
9.3^f
9.6^f
1.9
1.9
0.86
3.3
3.1
40^aIN THIS TABLE, PEO DENOTES THE ETHYLENE OXIDE REPEATING GROUP.^bFOLLOWING INTRODUCTION OF PG.^cFIGURE 5, 6 OR 7.^dFROM IR ABSORBANCE AND Li ANALYSIS.^eBASED ON APPROXIMATE THICKNESS OF 50 μm FOR FILMS 1-3; ON Li ANALYSIS FOR FILMS 4-8.^fMEASUREMENTS WITH IMPEDANCE METER.

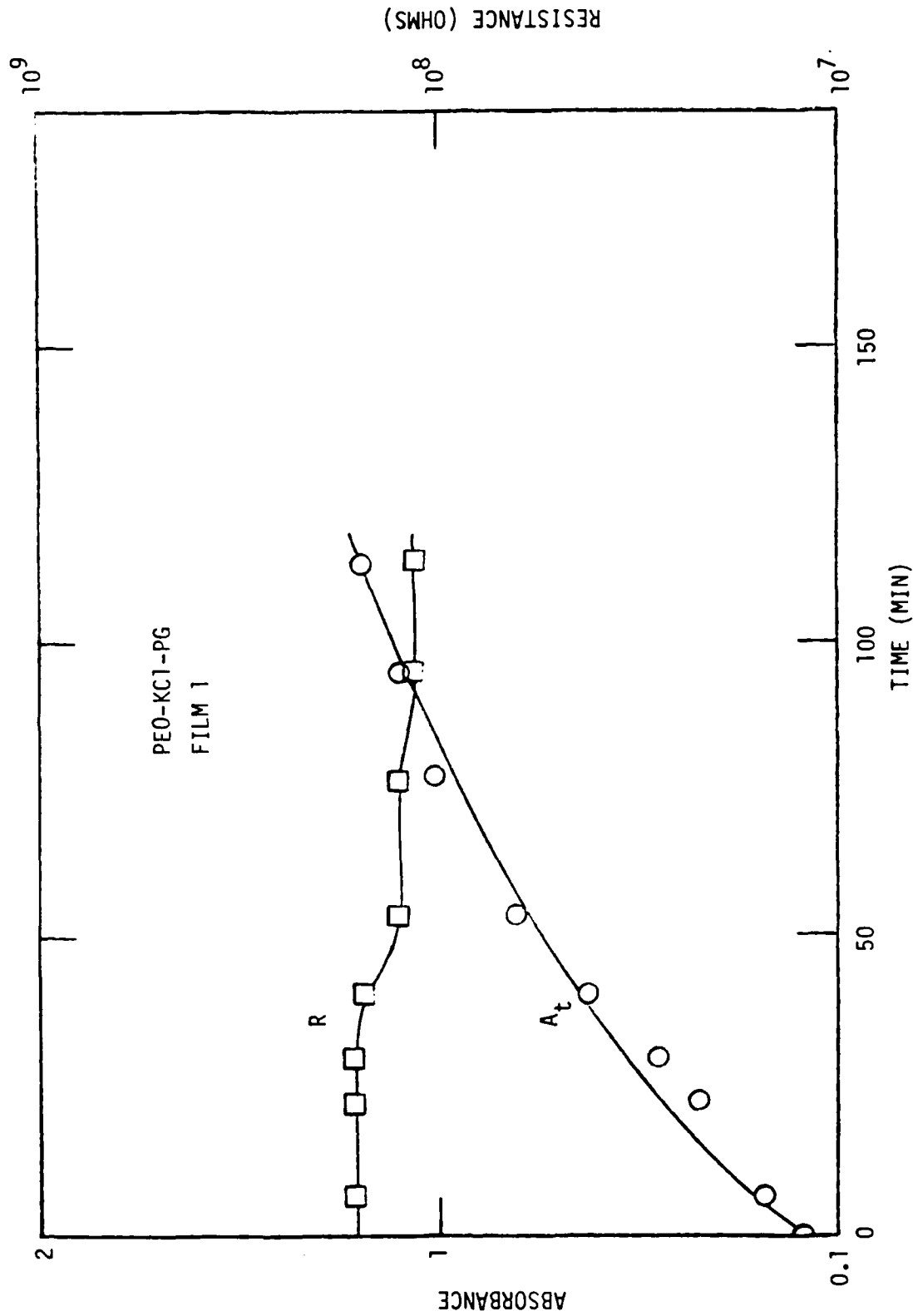


Figure 1. Variation of Resistance and Absorbance of PEO-KCl Film During Exposure to PG Vapor

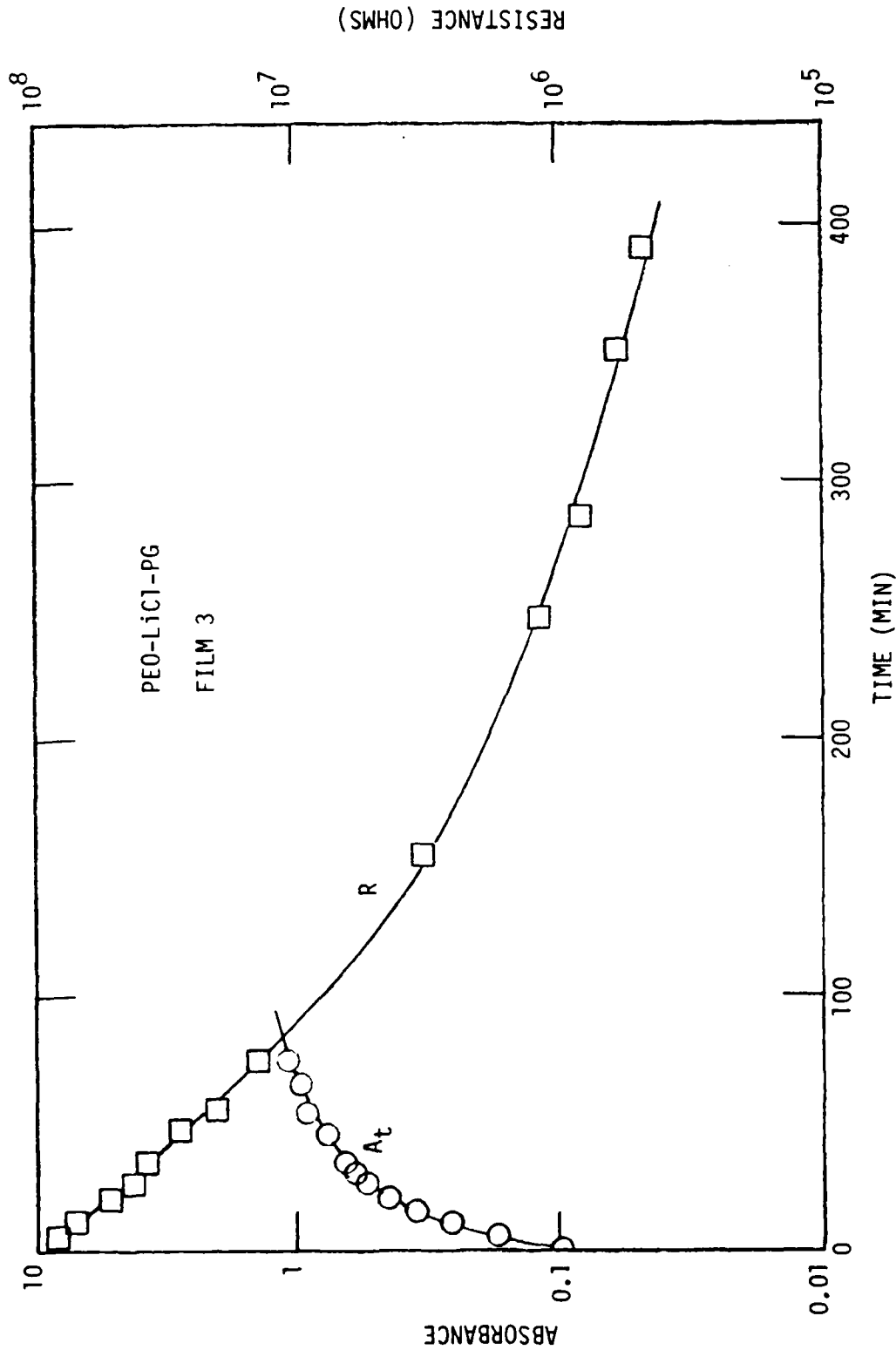


Figure 2. Variation of Resistance and Absorbance of PEO-LiCl Film During Exposure to PG Vapor

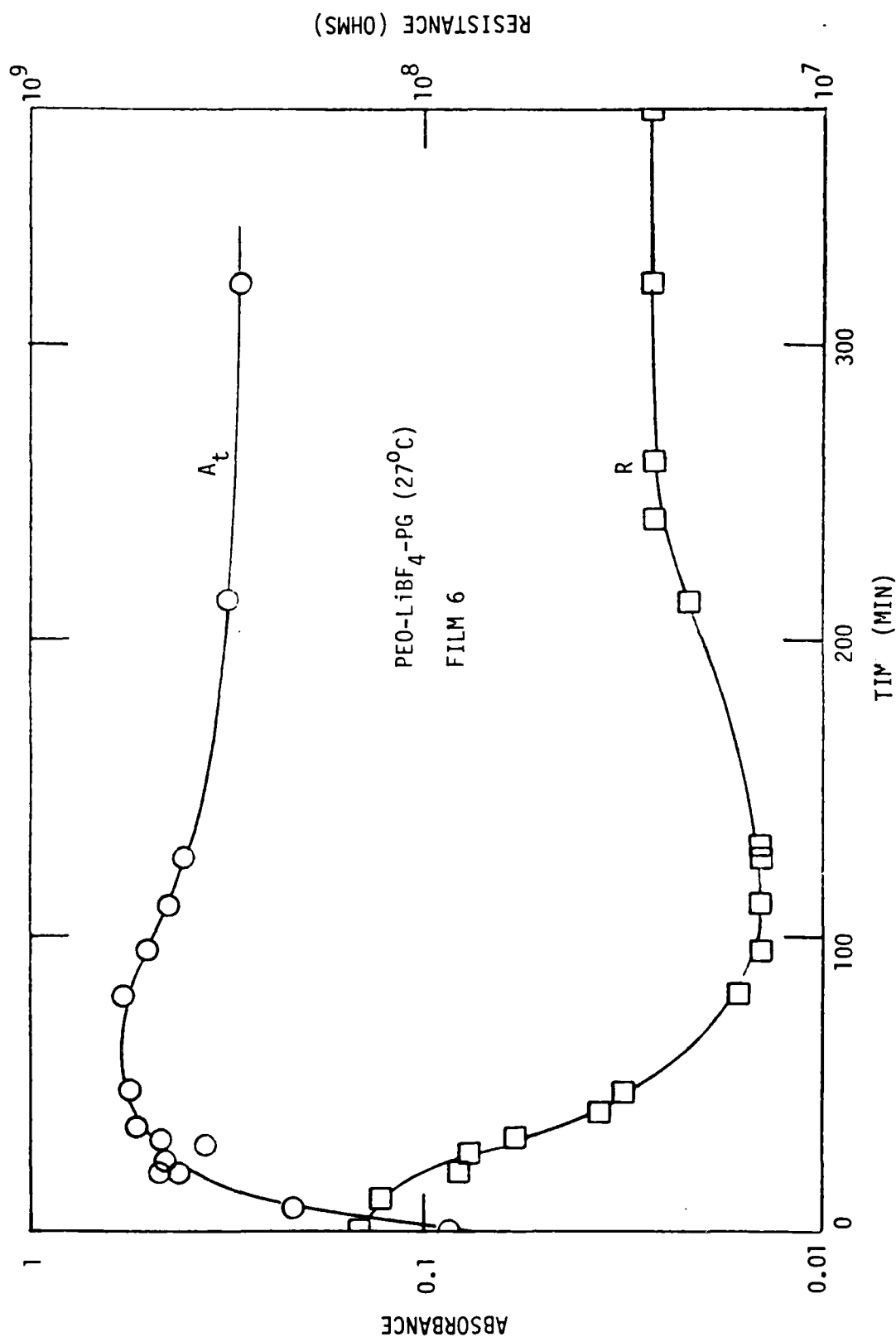


Figure 3. Variation of Resistance and Absorbance of PEO-LiBF₄ Film During Exposure to PG Vapor

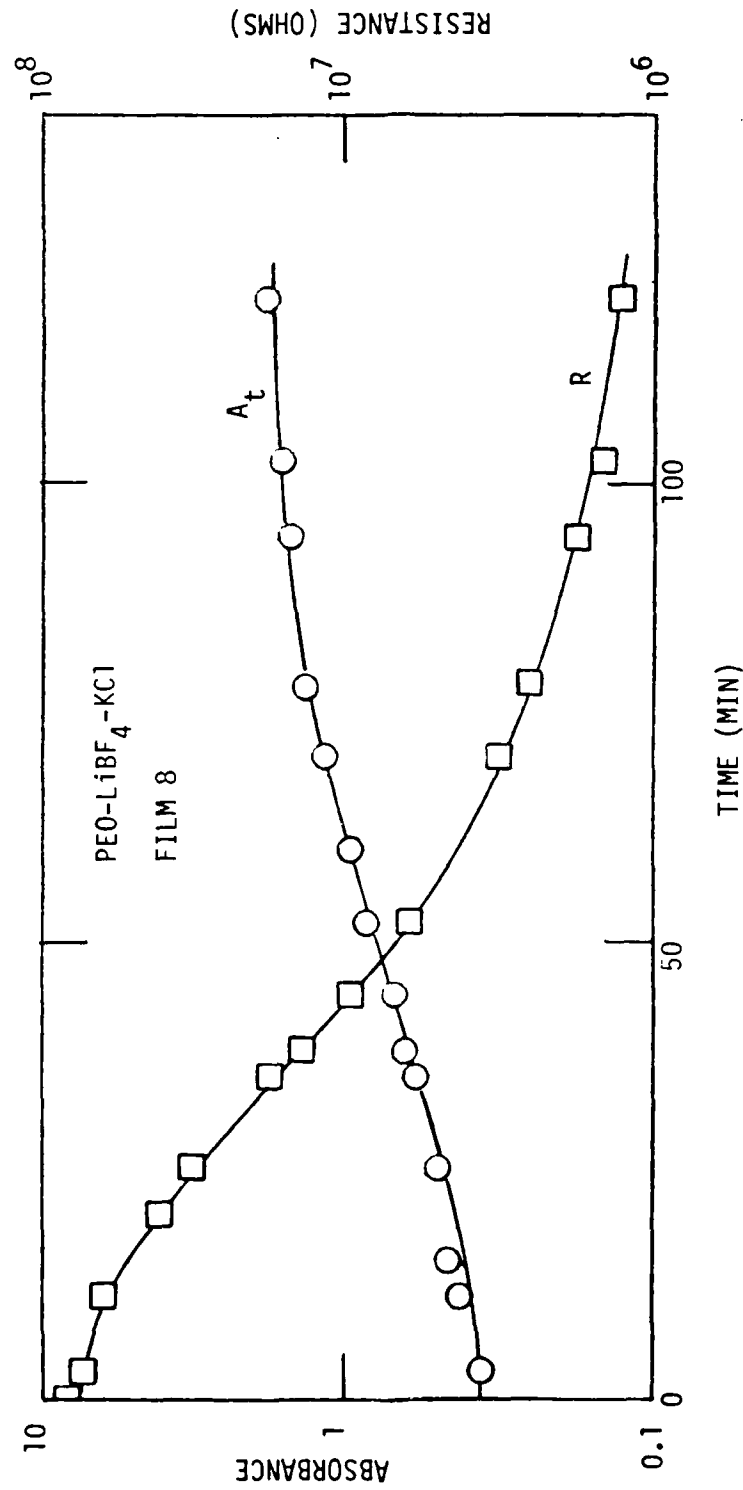


Figure 4. Variation of Resistance and Absorbance of PEO-LiBF₄-KCl Film During Exposure to PG Vapor

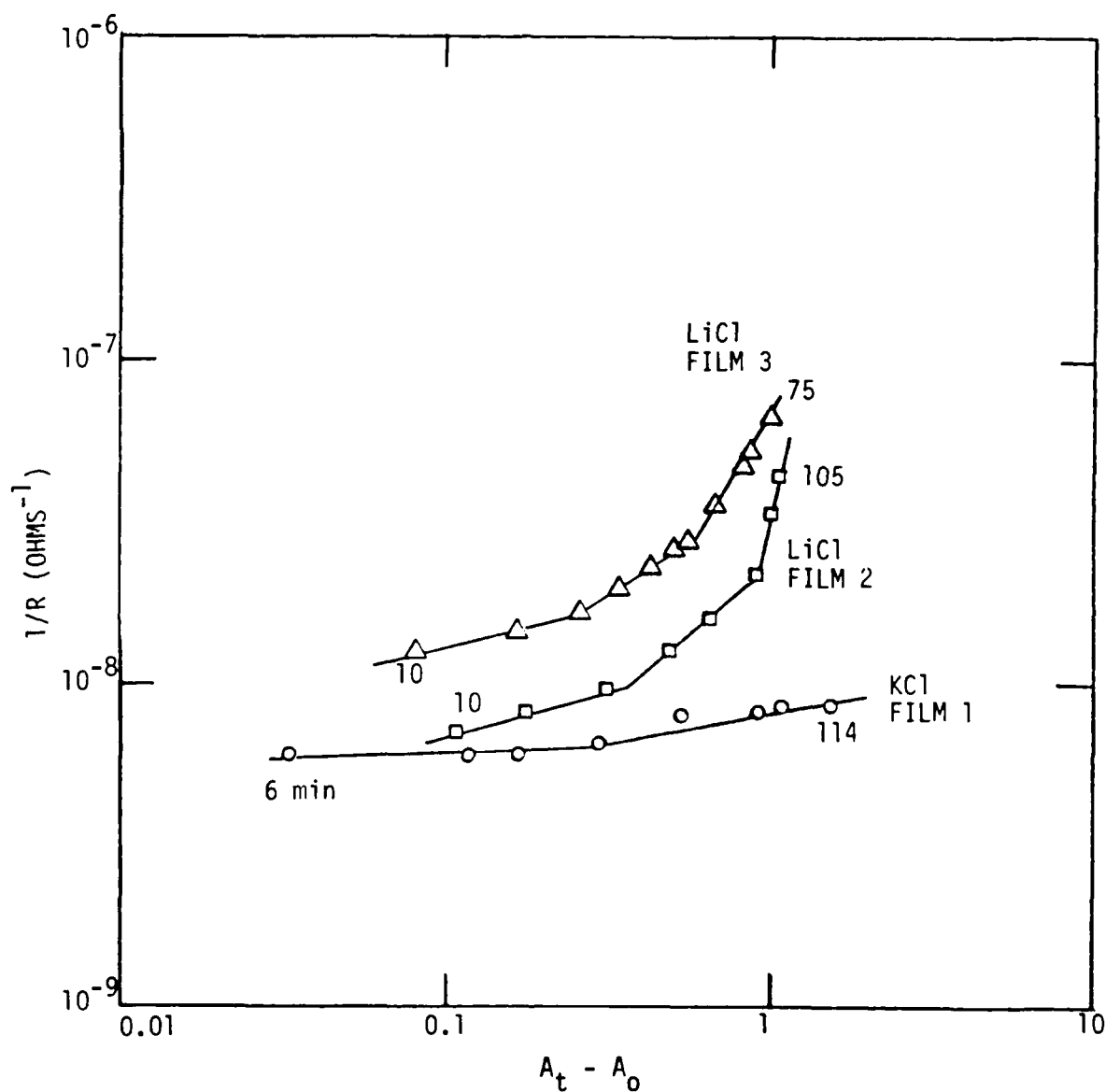


Figure 5. Dependence of Measured Conductance on Absorbance at Various Times in PEO-KCl and PEO-LiCl Films Exposed to PG Vapor

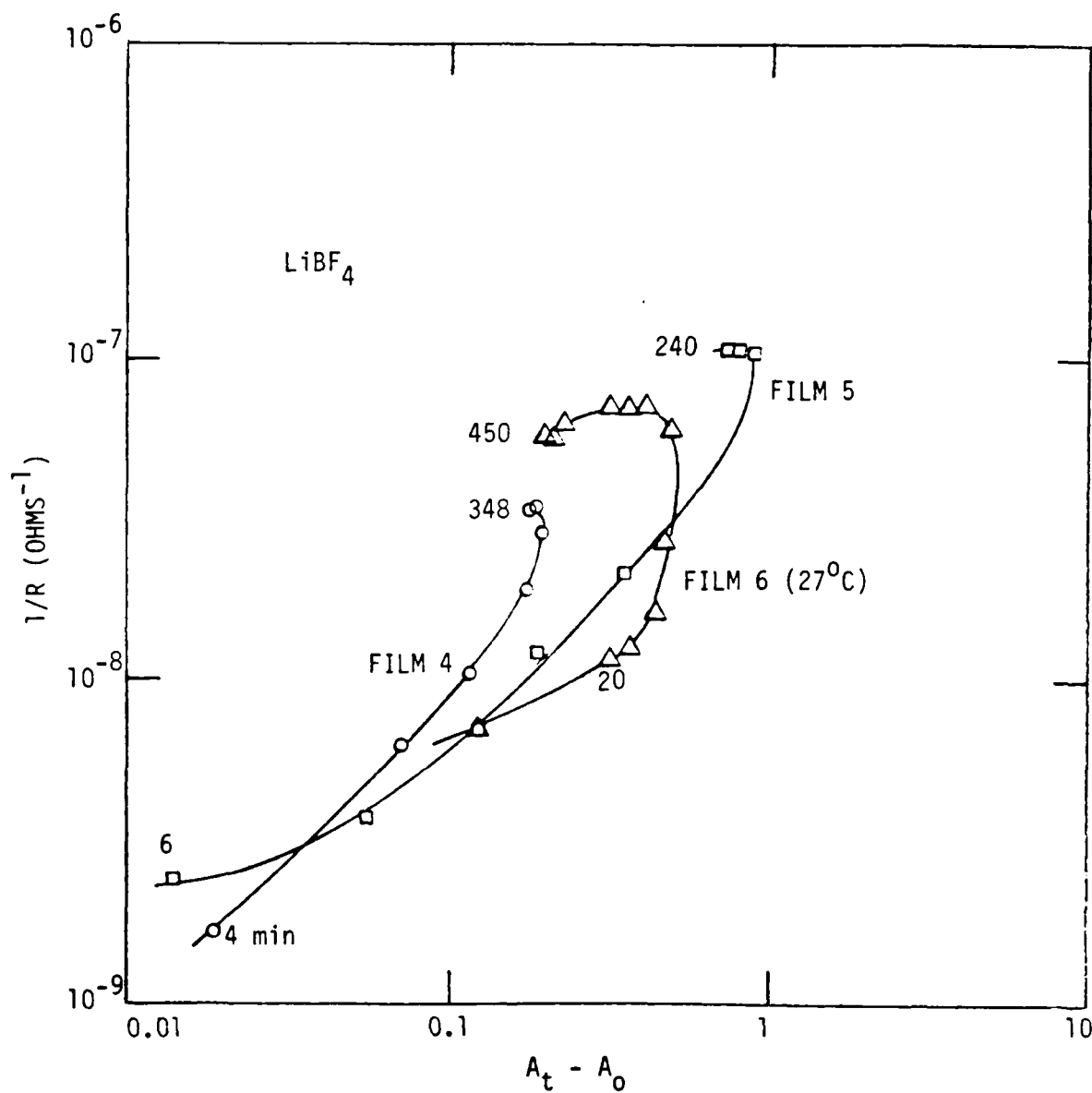


Figure 6. Dependence of Measured Conductance at Various Times in PEO- LiBF_4 Films Exposed to PG Vapor

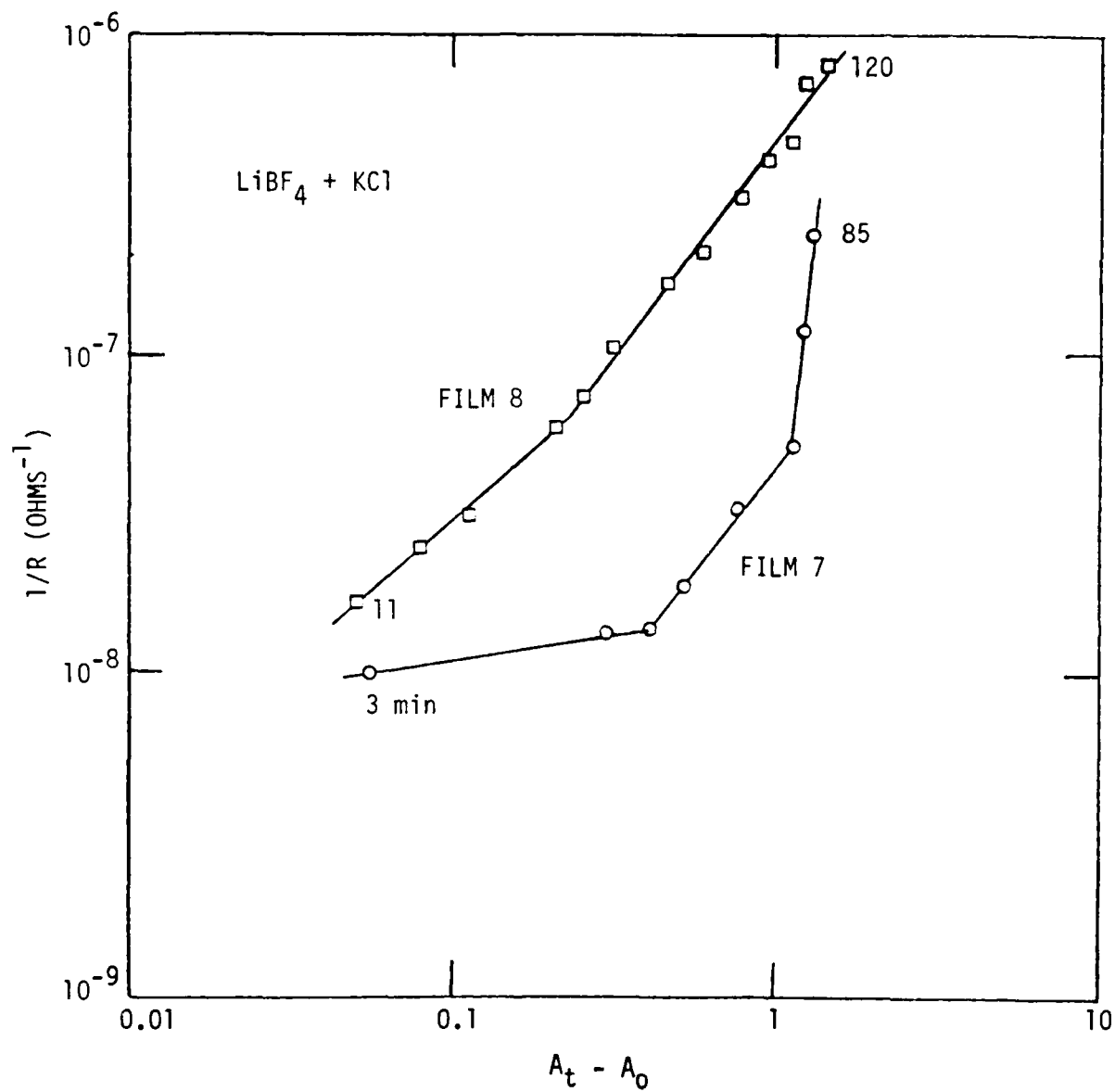


Figure 7. Dependence of Measured Conductance at Various Times in $\text{PEO-LiBF}_4\text{-KCl}$ Films Exposed to PG Vapor

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Duda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

END

DATE

3-88

DTIC