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TRANSPORT AND OPTICAL PROPERTIES OF POLYTHIAZYL BROMIDES.(U)
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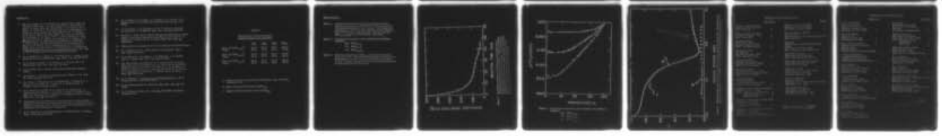

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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Transport and Optical Properties of Polythiazyl Bromides: $(SNBr_{0.4})_x$

by

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July 26, 1977

TRANSPORT AND OPTICAL PROPERTIES OF POLYTHIAZYL BROMIDES: $(SNBr_{0.4})_x$[†]

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ABSTRACT

Electrical transport and optical reflectance studies have been carried out on metallic derivatives of $(SN)_x$; $(SNBr_{0.4})_x$ and $(SNBr_{0.25})_x$. The average room temperature conductivity of $(SNBr_{0.4})_x$ is 3.8×10^4 $(\Omega\text{-cm})^{-1}$ with temperature dependence characteristic of metallic behavior. Resistance ratios depend on sample perfection. Analysis of the optical reflectance data for light polarized along the $(SN)_x$ chains yields $\hbar\omega_p = 4.8$ eV indicating little or no charge transfer upon bromination.

[†] This work was supported by the National Science Foundation by MRL program grant DMR 76-00678 and by grant CHE-73-04771-A03 and by the Office of Naval Research contract No. N00014-75-C-0962.

Polymeric sulfur nitride, polythiazyl, $(SN)_x$, has been of interest in recent years as the first example of a covalent polymer which is a metal. Studies of the optical and electronic properties have indicated metallic behavior along the $(SN)_x$ chains[1] with sufficient interchain coupling to give the properties of an anisotropic three dimensional metal.[2,3]

As part of a continuing study of the properties of $(SN)_x$ we have been investigating its reactions with halogens. In 1969 Patton[4] made brief reference to the fact that $(SN)_x$ reacts with chlorine to give NSCl. Bernard et al.[5] have reported recently that $(SN)_x$ reacts with bromine vapor at room temperature to give a gray-blue solid the composition of which was not determined. Independent studies carried out by us[6] and by Street et al.[7] involved the characterization of crystals and films of $(SNBr_{0.4})_x$, the first derivative of $(SN)_x$. In this paper we report[8] the initial results of studies of the electrical transport and optical properties of $(SNBr_{0.4})_x$ and the related derivative $(SNBr_{0.25})_x$.

Samples of polythiazyl bromides, $(SNBr_y)_x$, were prepared by reacting pure $(SN)_x$[9] with bromine vapor. For example, crystals of $(SN)_x$ (ca 1-10 mm^3) in 60 torr of bromine vapor react immediately at room temperature to give shiny black crystals having a lustrous blue-purple tinge. In order to determine the composition of the brominated material, a known weight of $(SN)_x$ was exposed to the bromine vapor and excess bromine was then removed from the product by pumping it for 5 to 15 minutes at room temperature. The weight of bromine absorbed was determined by weighing the polythiazyl bromide produced. The time required for the maximum amount of bromine to be absorbed under these conditions was approximately 40 minutes. The composition was confirmed by direct elemental analysis; compositions varied slightly, but significantly, according to minor variations in experimental procedure with values obtained for $(SNBr_y)_x$ in the range $0.38 \leq y \leq 0.42$. Two typical analyses are given in Table 1. For convenience, this material will be referred to as $(SNBr_{0.4})_x$ in this paper. No unreacted $(SN)_x$ could be detected visually or in the x-ray powder patterns of the material. Crystals of $(SNBr_{0.4})_x$ appear to react with air to a negligible extent during one hour at room temperature but are tarnished after 10 hours during which time some ammonium bromide is formed.

Other compositions besides $(SNBr_{0.4})_x$ can also be synthesized. Crystals which were weighed under 60 torr of bromine vapor had a bromine content as high as $(SNBr_{0.55})_x$. Material containing even less bromine, e.g. $(SNBr_{0.05})_x$ was prepared by reacting $(SN)_x$ with bromine for shorter periods and/or at lower bromine vapor pressures. However, some of these compositions may contain some unreacted $(SN)_x$ and will not be discussed further. When crystals of $(SNBr_{0.4})_x$ were pumped at room temperature for 45 hours or more, there was little change in appearance, but the bromine content decreased to as low as $(SNBr_{0.33})_x$. When crystals of $(SNBr_{0.4})_x$ were heated with pumping at approximately 86° C for about 30 hours they were converted to copper-colored crystals with composition $(SNBr_{0.25})_x$ (See Table 1), and density (2.52 ± 0.04 g/cm^3).

The density of the $(SNBr_{0.4})_x$ (2.67 ± 0.04 g/cm^3) is significantly greater than that of $(SN)_x$ (2.30 g/cm^3).[6,7] The volume increase calculated from the formula and density data is 46%, in reasonable agreement with the observed changes in crystal dimensions upon bromination.[6,7] There is no significant change in the length of the crystal in the b crystallographic direction (the direction parallel to the $(SN)_x$ polymer chains).[6,7] The entire volume change results from a swelling of the crystal perpendicular to the chain axis. Although the crystals appear well-formed, X-ray studies show they have very considerable defect structure. The fibrous nature characteristic of $(SN)_x$ crystals when mechanically pulled apart is preserved in $(SNBr_{0.4})_x$.

To monitor the kinetics of the chemical reaction and provide definitive data on the change in electrical resistance on bromination, we have measured the resistance along the chain axis during the bromination of a single crystal of $(SN)_x$. The resulting normalized resistance vs. time during the reaction is shown in Figure 1. The data were obtained in bromine vapor at a pressure of 20-25 torr. Chemical analysis of crystals brominated in the same experiment showed the reaction had proceeded to give the composition $(SNBr_{0.40})_x$. Contacts to the sample were made with the graphite suspension Electrodag (Acheson Colloid Co., Port Huron, Mich.) in order to avoid reaction of the usual metallic contacts. The measurements were made using four-probe low frequency (37 Hz) ac techniques.

The initial reaction proceeds rapidly and results in an obvious decrease in the sample resistance. The resistance eventually falls to a value approximately 0.05 of the initial value as shown in Figure 1. Taking into account the ~46% increase in cross-sectional area, we find a final room temperature conductivity approximately 13 times the initial $(SN)_x$ value. Independent measurements on five samples of $(SNBr_{0.4})_x$ mounted for measurement after reaction yielded values from 1.4×10^4 to 9.1×10^4 $(\Omega\text{-cm})^{-1}$ with an average room temperature conductivity, $\sigma_{\|}(300\ K) = 3.8 \times 10^4\ (\Omega\text{-cm})^{-1}$. Room temperature measurements of $\sigma_{\perp}$ yielded $8\ (\Omega\text{-cm})^{-1}$, i.e. comparable to the values obtained for pure $(SN)_x$. However, because of the fibrous nature of the crystals, the value for $\sigma_{\perp}$ is probably not intrinsic but is determined by inter-fibre contact.

The temperature dependence of the resistivity of $(SNBr_{0.4})_x$ along the chain axis is shown in Figure 2. The data were obtained using four-probe dc techniques with Electrodag contacts. The normalized results for two samples shown in Figure 2 indicate metallic behavior over the entire temperature range T < 300 K. Sample 1 (closed circles) had room temperature conductivity of $9.1 \times 10^4\ (\Omega\text{-cm})^{-1}$ and a resistance ratio $\rho(300\ K)/\rho(4.2\ K) \simeq 90$. Sample 2 (open circles) had room temperature conductivity of $1.4 \times 10^4\ (\Omega\text{-cm})^{-1}$ and a resistance ratio of approximately

12. Note that sample 2 becomes residual at T ≥ 10 K whereas the resistivity of sample 1 continues to decrease becoming residual at a value $\rho_o \simeq 1.2 \times 10^{-7}$ (Ω-cm) only well below 10 K.

The temperature dependence of the resistivity of a crystal of $(SNBr_{0.25})_x$ is also shown on Figure 2 for comparison. The results again indicate metallic behavior with typically somewhat larger residual resistivity values. Measurements on six samples of $(SNBr_{0.25})_x$ yielded an average room temperature conductivity of 2×10^4 $(\Omega\text{-cm})^{-1}$ with values ranging from 0.9×10^4 to 5.9×10^4 $(\Omega\text{-cm})^{-1}$.

Attempts to analyze the temperature dependence as $\rho = \rho_o + AT^n$ yielded $1 < n < 2$ for both $(SNBr_{0.4})_x$ and $(SNBr_{0.25})_x$. However, log-log plots suggest that a single power law is inadequate to describe the data. The temperature dependence of the brominated material is somewhat weaker than the well-defined T^2 behavior[10] found in $(SN)_x$.

Upon bromination, $(SN)_x$ crystals change color from the characteristic highly reflecting golden appearance to black crystals of $(SNBr_{0.4})_x$ having a blue-purple tinge. To examine this quantitatively, we have carried out polarized reflectance measurements from single crystals of $(SNBr_{0.4})_x$. The results are shown in Figure 3. The reflectance spectrum for light polarized along the principal conducting axis ($R_{||}$) shows a broad minimum in the visible with a plasma edge $\hbar\omega_p/(\epsilon_\infty)^{\frac{1}{2}}$ and high reflectivity in the near infrared. The plasma edge is shifted from approximately 2.55 eV in $(SN)_x$ to about 1.65 eV for $(SNBr_{0.4})_x$. For light polarized perpendicular to the principal conducting axis, the reflectance ($\mathcal{R}_{\perp}$) is flat and featureless with no sign of metallic behavior ($\mathcal{R}_{\perp} \sim 3\%$ over the entire range). The long wavelength optical anisotropy of $(SNBr_{0.4})_x$ is greater than that of $(SN)_x$ indicating somewhat weaker interchain coupling. Polarized reflectance data have also been obtained from oriented films of brominated $(SN)_x$ on Mylar. The results are consistent with the single crystal data.

Below 1 eV, $\mathcal{R}_{\parallel}$ decreases rather than asymptotically approaching 100% as would be the case for a simple Drude dielectric function. Since the dc conductivity is high, the most likely explanation involves a relatively strong low frequency interband transition with corresponding structure in $\epsilon(\omega)$. Similar effects have been observed in graphite intercalation compounds.$^{(11)}$ Alternatively, the decrease may result from structure in $\epsilon(\omega)$ arising from a pseudogap related to the more nearly one-dimensional behavior suggested by the optical anisotropy. Detailed reflectance measurements into the intermediate and far ir regions will be required to develop a complete picture of the dielectric function. Our initial studies presented here focus on the oscillator strength and comparison of $(SNBr_{0.4})_x$ with $(SN)_x$.

The $(SNBr_{0.4})_x$ reflectance data, $\mathcal{R}_{\parallel}$, were analyzed in the vicinity of the plasma edge assuming a simple Drude dielectric function

$$\epsilon(\omega) = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\,\omega/\tau}$$

where ϵ_∞ represents the combined contributions from high frequency interband transitions and the core atomic polarizabilities, τ is the conduction electron scattering time, $\omega_p = (4\pi Ne^2/m^*)^{\frac{1}{2}}$ is the plasma frequency, and N is the number of conduction electrons per unit volume with optical effective mass m^*. The solid curve on Figure 3 represents a least-square fit (weighted by $\mathcal{R}^{-\frac{1}{2}}$) arbitrarily restricting the input data to the range above 1.1 eV. The resulting parameters are $\hbar\omega_p = 4.8$ eV, $\epsilon_\infty = 8.7$ and $\hbar/\tau \simeq 0.4$ eV. Because of the clear deviation from Drude behavior below 1 eV, these parameters can be taken only as an indication of overall behavior. Nevertheless, it is instructive to compare the results with the corresponding values for $(SN)_x$, of $\hbar\omega_p = 5.1$ eV, $\epsilon_\infty^b = 4.2$ and $\hbar/\tau = 0.55$ eV.[12] The small decrease in plasma frequency is more than accounted for by the ~ 46% increase in sample volume on bromination indicating that any charge transfer to the bromine acceptor states is weak. The downward shift in plasma edge $\hbar\omega_p/(\epsilon_\infty)^{\frac{1}{2}}$ on bromination appears to be primarily due to the larger value for ϵ_∞.[13]

Visual observation of the crystals after reaction suggests that bromination decreases the crystalline quality. X-ray studies confirm these latter observations. The brominated material is crystalline; however, the relatively well-defined x-ray patterns obtained from $(SN)_x$ crystals become broad and diffuse indicative of a significant decrease in crystal quality. Nevertheless, the dc conductivity studies described above demonstrate an increase in the absolute value of conductivity with resistance ratios comparable to those found in relatively high quality $(SN)_x$. The reflectance data from $(SNBr_{0.4})_x$ indicate no significant change in (N/m^*) compared with $(SN)_x$ and a value for $\hbar/\tau$ comparable to that typically found for $(SN)_x$ ($\sigma_{opt} = \frac{1}{4\pi}\omega_p^2\tau \simeq 7000\,(\Omega\text{-cm})^{-1}$). These results therefore provide evidence that the fundamental $(SN)_x$ chains remain intact as bromine enters the structure with little or no charge transfer. The combined transport and optical data suggest an analogy with bromine intercalation compounds of graphite.[14]

The observation of little or no charge transfer from $(SN)_x$ to bromine is consistent with the known electronegativities. The Pauling electronegativity of bromine (2.8) is equal to the average of the electronegativities of sulfur (2.5) and nitrogen (3.0). The possibility that charge transfer might occur <u>from</u> the bromine <u>to</u> the $(SN)_x$ chain may even be considered. In this case, the charge transfer would tend to compensate for the reduction in electron density caused by the increase in volume of the $(SN)_x$ upon bromination. This is consistent with the suggestion from Schottky barrier studies[15] that $(SN)_x$ may be assigned an effective electronegativity of 2.9 or more on the Pauling scale.

The observation of more than an order of magnitude increase in room temperature conductivity upon bromination is particularly interesting in the context of the optical properties and the poorer overall crystal quality. Earlier measurements[10] of the temperature dependence of the conductivity of pure $(SN)_x$ indicated that $\rho \propto T^2$ over a wide range of temperatures. Band structure calculations[16] characterized $(SN)_x$ as a semi-metal in which the resistivity may be dominated by electron-electron scattering processes[10,17] leading to a T^3 term in the resistivity with magnitude which is sensitive to detailed features of the electron and hole pieces of the Fermi surface. The higher conductivity and weaker temperature dependence of $(SNBr_{0.4})_x$ compared to $(SN)_x$ imply that the T^3 contribution is smaller in the brominated compound. Evidently the combined effects of a small change in (N/m^*) and the implied decrease in interchain coupling as inferred from the optical studies partially quench the T^3 contribution. Such effects have been predicted from analysis of electron-hole scattering in semi-metals[18] and have been observed in non-stoichiometric TiS_2.[19]

In summary, ~~out~~ our initial transport and optical studies of this class of brominated derivatives of $(SN)_x$, polythiazyl bromides, demonstrate metallic behavior. The $(SN)_x$ chains appear to remain intact with somewhat weaker interchain coupling as inferred from the optical anisotropy. The bromine evidently enters the structure with little or no charge transfer. The relatively high room temperature conductivity, $\sigma(300\ K) \simeq 4 \times 10^4\ (\Omega\text{-cm})^{-1}$, in highly defected crystals of $(SNBr_{0.4})_x$ is encouraging from the point of view of the eventual possibility of useful highly conducting synthetic polymers.

Acknowledgement: We thank Dr. A. J. Epstein for helpful suggestions on achieving stable contacts in the presence of bromine.

References:

1. See, for example, V. V. Walatka, Jr., M. M. Labes, and J. H. Perlstein, Phys. Rev. Lett. 31, 1139 (1973); C. Hsu and M. M. Labes, J. Chem. Phys. 61, 4640 (1974); C. M. Mikulski, P. J. Russo, M. S. Saran, A. G. MacDiarmid, A. F. Garito and A. J. Heeger, J. Amer. Chem. Soc. 97, 6358 (1975); R. L. Greene, P. M. Grant, and G. B. Street, Phys. Rev. Lett. 34, 89 (1975); R. L. Greene, G. B. Street, and L. J. Suter, Phys. Rev. Lett. 34, 577 (1975); M. J. Cohen, A. F. Garito, A. J. Heeger, A. G. MacDiarmid, C. M. Mikulski, M. S. Saran and J. Kleppinger, J. Amer. Chem. Soc. 98, 3844 (1976); R. H. Baughman, P. A. Apgar, R. R. Chance, A. G. MacDiarmid and A. F. Garito, J. Chem. Phys. 66, 401 (1977); H. P. Geserich and L. Pintschovius, in Festkörperprobleme (Advances in Solid State Physics), Vol. XVI, p. 65, J. Treusch (ed.), Vieweg, Braunschweig (1976).

2. A. A. Bright, M. J. Cohen, A. F. Garito and A. J. Heeger, C. M. Mikulski and A. G. MacDiarmid, Appl. Phys. Lett. 26, 612 (1975).

3. C. H. Chen, J. Silcox, A. F. Garito, A. J. Heeger, and A. G. MacDiarmid, Phys. Rev. Lett. 36, 525 (1976)

4. R. L. Patton, Ph.D. Thesis, University of California, Berkeley, (1969)

5. C. Bernard, A. Herold, M. Lelaurain and G. Robert, C. R. Acad. Sc. Paris, C, 283, 625 (1976)

6. M. Akhtar, J. Kleppinger, A. G. MacDiarmid, J. Milliken, M. J. Moran, C. K. Chiang, M. J. Cohen, A. J. Heeger and D. L. Peebles, Chem. Commun. in press.

7. G. B. Street, W. D. Gill, R. H. Geiss, R. L. Greene and J. J. Mayerle, Chem. Commun., in press; W. D. Gill, W. Bludau, R. H. Geiss, P. M. Grant, R. L. Greene, J. J. Mayerle, and G. B. Street, Phys. Rev. Lett. 38, 1305 (1977)

8. A preliminary version of this study was presented as a post-deadline contributed paper at the American Physical Society Meeting, San Diego, California, March 23, 1977. Similar results were reported at the same meeting by G. B. Street et al. (see ref. 7).

9. C. M. Mikulski, A. G. MacDiarmid, A. F. Garito and A. J. Heeger, Inorg. Chem. 15, 2943 (1976)

10. C. K. Chiang, M. J. Cohen, A. F. Garito, A. J. Heeger, C. M. Mikulski and A. G. MacDiarmid, Solid State Commun. 18, 1451 (1976)

11. J. E. Fischer, T. E. Thompson, G. M. T. Foley, D. Guerard, M. Hoke and F. L. Lederman, Phys. Rev. Lett. 37, 769 (1976)

12. Marshall J. Cohen, Ph. D. Thesis, University of Pennsylvania (1975). Similar results have been obtained for $(SN)_x$ by others; see P. M. Grant, R. L. Greene, and G. B. Street, Phys. Rev. Lett. 35, 1743 (1975)

13. This point has been emphasized by W. D. Gill; private communication.

14. D. A. Platts, D. D. L. Chung and M. S. Dresselhaus, Phys. Rev. B 15, 1087 (1977)

15. R. A. Scranton, J. B. Mooney, J. O. McCaldin, T. C. McGill and C. A. Mead, Appl. Phys. Lett. 29, 46 (1976)

16. See, for example, the following: W. E. Rudge and P. M. Grant, Phys. Rev. Lett. 35, 1799 (1975); A. A. Bright and P. Soven, Sol. State Commun. 18, 317 (1976); M. Schlicter, J. R. Chelikowski and M. L. Cohen, Phys. Rev. Lett. 35, 869 (1975); W. I. Freisen, A. J. Berlinsky, B. Bergersen, L. Weiler, and T. M. Rice, J. Phys. C8, 3549 (1975)

17. A. A. Abrikosov, *Introduction to the Theory of Metals*, p. 67-73 (Academic Press, New York (1972)).

18. C. A. Kukkonen and P. F. Maldague, Phys. Rev. Lett. 37, 782 (1976)

19. A. H. Thompson, Phys. Rev. Lett. 35, 1786 (1975); and private communication.

TABLE I

Representative Elemental Analyses of Selected Polythiazyl Bromides[a]

	%S	%N	%Br	Total
Calc. for $(SNBr_{0.40})_x$[b]	41.09	17.95	40.96	100.00
Found	40.92	17.93	41.01	99.86
Calc. for $(SNBr_{0.38})_x$[b]	41.95	18.32	39.73	100.00
Found	42.10	18.15	39.85	100.10
Calc. for $(SNBr_{0.25})_x$[c]	48.54	21.21	30.25	100.00
Found	48.34	21.06	30.25	99.65

a. Analyses performed by Galbraith Laboratories, Inc., Knoxville, Tennessee 37921.

b. Shiny, black crystalline form of $(SNBr_y)_x$.

c. Copper-colored crystalline form of $(SNBr_y)_x$.

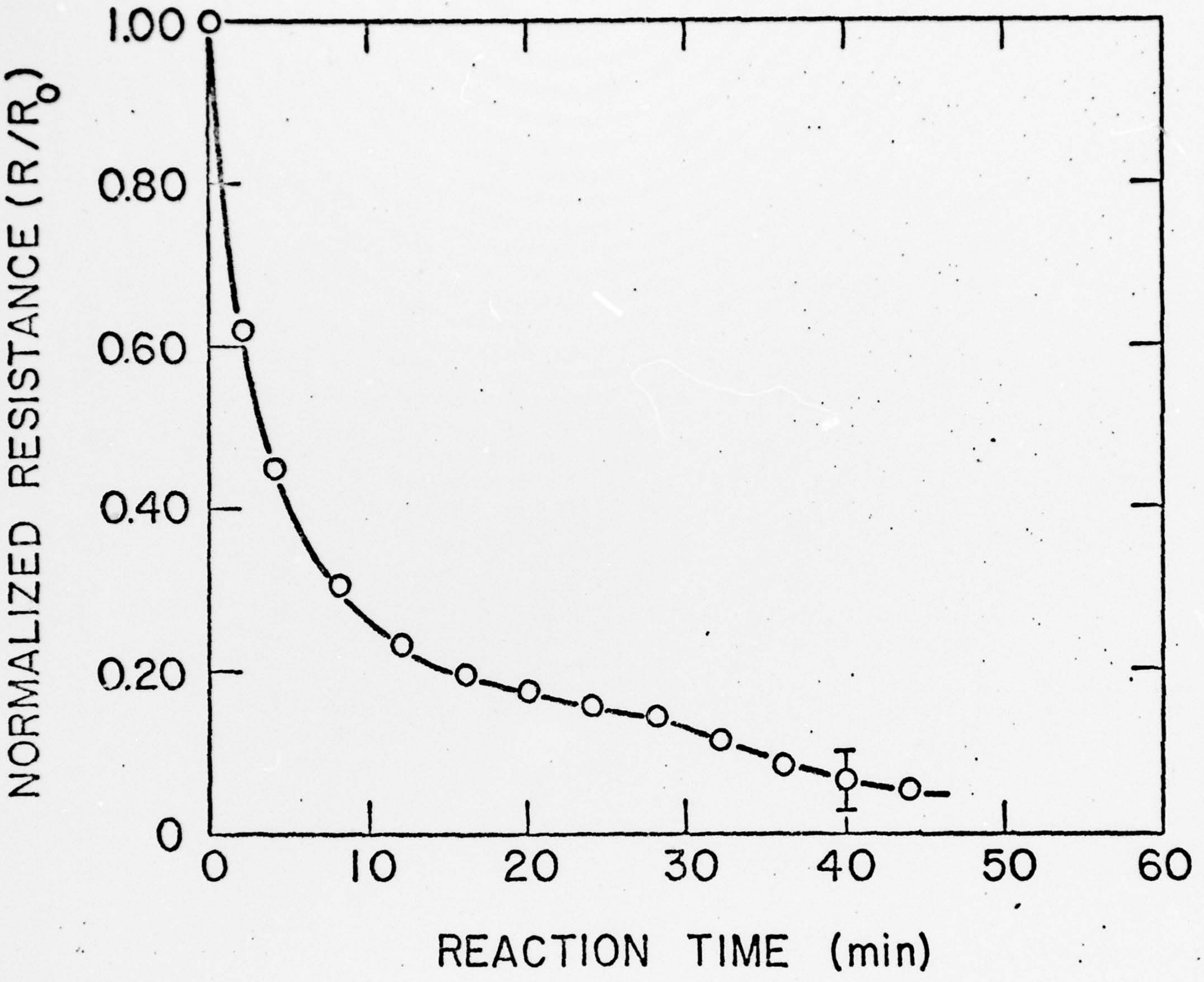
Figure Captions:

Figure 1. Normalized resistance of $(SNBr_y)_x$ during bromination; bromine vapor pressure of 20-25 Torr. Chemical analysis of the product indicated y = 0.4; see text. The sample conductivity was 1.6×10^3 $(\Omega\text{-cm})^{-1}$ before reaction increasing to 2.2×10^4 $(\Omega\text{-cm})^{-1}$ after reaction. Average value for $SNBr_{0.4}$; $\sigma_{(300K)} = 3.8 \times 10^4$ $(\Omega\text{-cm})^{-1}$ (see text).

Figure 2. Temperature dependence of the resistivity of polythiazyl bromides;

●●● $(SNBr_{0.4})_x$
ooo $(SNBr_{0.4})_x$
+++ $(SNBr_{0.25})_x$

Figure 3. Polarized reflectance of $(SNBr_{0.4})_x$ in the spectral range 0.6 eV to 2.5 eV. The solid curve represents a least-square fit arbitrarily restricting the input data to the range above 1.1 eV. The data are plotted using the absolute normalization as determined from the Drude fits.



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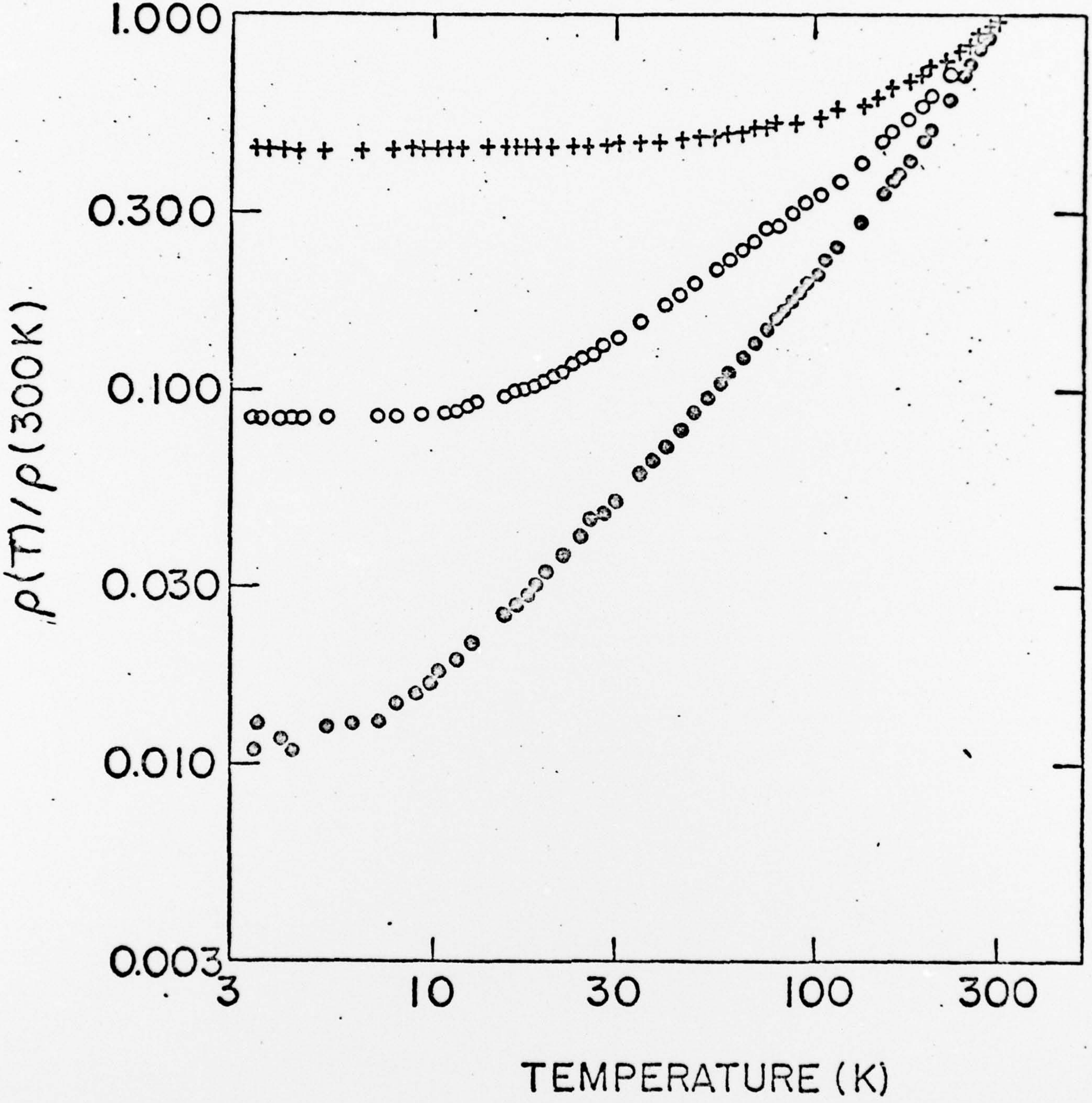

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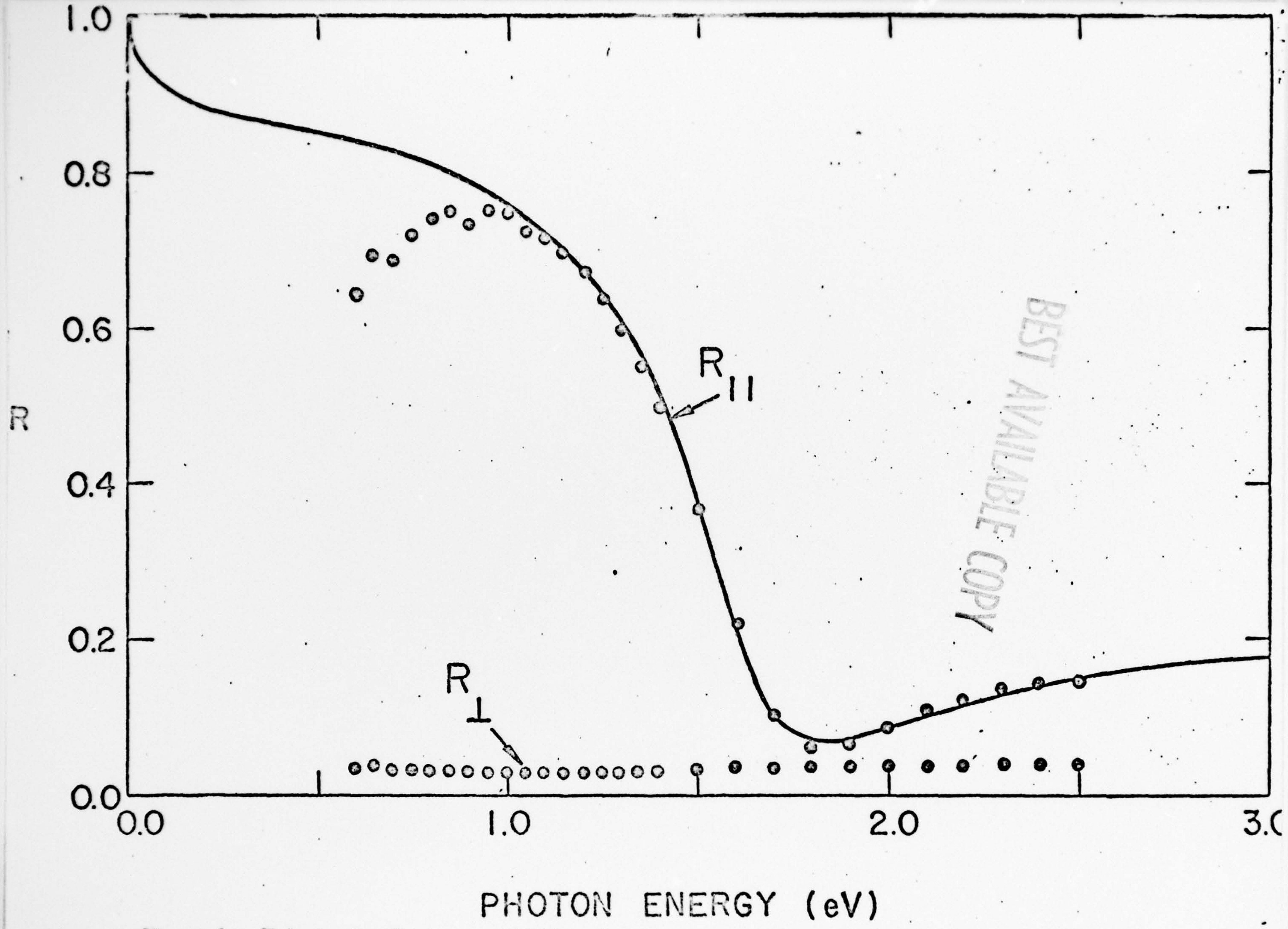

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