NASA-TM-77975 19860012156

NASA TECHNICAL MEMORANDUM

NASA TM-77975

Electrical Photosemiconducting and Paramagnetic Properties of Polypromellitimides

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Translation of Elektricheskiye Fotopoluprovodnikovyye i paramagnitnyye svoystva polipiromellitimidov, Vysokomolekuliarnye Soedineniia, Series B, Vol. 16, No. 4, 1974, pp. 295-298

Title varies: Vysokomolekuliarnye Soedineniya, Seriya B: Kratkie Soobshcheniya

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 DECEMBER 1985

STANDARD TITLE PAGE

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-77975		

4. Title and Subtitle	5. Report Date
Electrical Photosemiconducting and Paramagnetic Properties of Polypromellitimides	December 1985
	6. Performing Organization Code
7. Author(s)	8. Performing Organization Report No.
Voishchev, V.S. et al	
	10. Work Unit No.
9. Performing Organization Name and Address	11. Contract or Grant No.
Leo Kanner Associates Redwood City, Ca. 94063	NASW-4005
	12. Type of Report and Period Covered
12. Sponsoring Agency Name and Address	Translation
National Aeronautics and Space Administration, Washington, D.C. 20546	14. Sponsoring Agency Code

15. Supplementary Notes

Translation of Electricheskiye Fotopoluprovodnikovyye i paramagnitnyye svoystva polipiromellitimidov, Vysokomolekuliarnye Soedineniia, Series B, Vol. 16, No. 4, 1974, pp. 295-298 (UDC 541 {64+67}:538.113)

16. Abstract

Semiconducting properties with dark and photoconductivity, type r, were observed in PPMI and explained by a donor-acceptor interreaction in the PPMI between electron acceptor promellitimide fragments and electron donor diamide in adjacent macromolecules.

17. Key Words (Selected by Author(s))	18. Distribution Statement
	Unclassified- Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22.
Unclassified	Unclassified	4	

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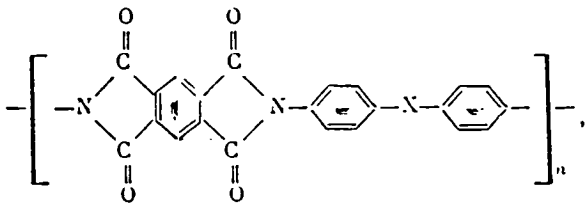
As part of the continuing research on the properties of aromatic polyheteroarylenes as a function of their structure, this paper examines certain physical properties of polypromellitimides (PPMI)



where X=-O-(PM), -S-(DDS), -NH-(DDA).

Although PPMI conductivity has been studied in depth, little has been reported on the photoelectric phenomena of these polymers. Research on PPMI photoelectric properties is needed to determine their photoelectric sensitivity as well as to provide a better understanding of the electron phenomena, occuring in these systems.

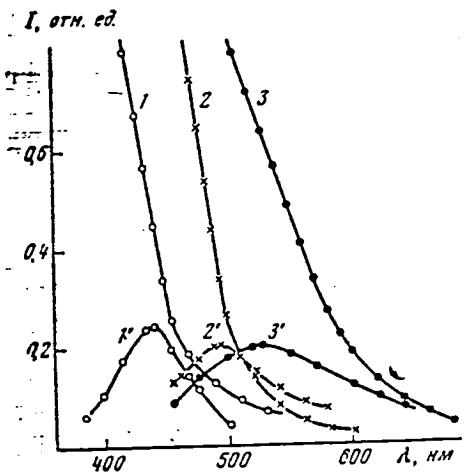
Methodology

The samples were films, 5-15mcm in thickness, with silver electrodes applied by vacuum spraying. Surface preparation of the films and means of obtaining PPMI of a given chemical structure have been described in earlier papers (1,3). It should be noted, that prior to the experiment the samples were heated at 300° for 1 hour in a vacuum ($\sim 10^{-3}$ tor) directly in the measuring cell to eliminate absorbed moisture, and then dried and purified of argon in the chamber. The procedure used to determine the concentration N of the paramagnetic centers (PMC) has been noted earlier (4). Photoelectric properties of the samples were studied (photo-EMF and direct current photoconductivity) in a vacuum ($\sim 10^{-3}$ tor), by using an illuminator, consisting of a xenon lamp type DKSSH-1000 and monochromator type ZMR-3. Voltage of the thermo-EMF (electro-

motive force) was measured by a high-resistance amplifier type UI-2, with an impedance of $1 \cdot 10^{11}$ ohm. Since the polymers were high-resistance materials, we were only able to determine the sign of the thermo-EMF.

Discussion of Results

Research on dark conductivity and optic absorption spectra of PPMI with various chemical structures showed that they have semiconducting properties, which are characteristic of polymers. The photoelectric properties of PPMI were also studied and the results were correlated with known measurements for dark conductivity. All of the poliimides had photoelectric sensitivity in the visible range. The curves for photocurrent spectrum pattern are shown in the drawing. Photocurrent peaks are found on the slopes of the corresponding absorption curves. Wavelengths for the photocurrent peaks (λmax) are found in the table below.



Spectra absorption curves (1-3) and photocurrent curves for unit of decreasing energy (1'-3') for PPMI of various structures: 1,1'-PM, 2,2'-DDS 3,3'-DDA

Conductivity and Photoconductivity for Polypromellitimides

Polymer	X	ΔE_T, eV	E_{opt}, eV	$E_{\lambda_{max}}$, eV	$\lg\sigma_D$*, ohm^{-1}·cm^{-1} at 200°	λ_{max}	Sign	
							photo-EMF	thermo-EMF
PM	—O—	2.60	2.63	2.65	14.95	440	+	+
DDS	—S—	2.42	2.42	2.40	14.36	500	+	+
DDA	—NH—	2.14	1.98	2.16	13.22	325	+	+

* $\lg\sigma_D$ —

During the replacement of -O- by -S- and -NH- max is shifted to the longwave side. The photoconducting threshold ($E_{\lambda_{1/2}}$), which was determined by Moss's procedure, decreases in order -O-, -S-, -NH-. The coincidence in measurement error should be noted for the activation energy values for dark conductivity ($2E_t$), minimal photon energy which corresponds to the edge of optic absorption (E_{opt}), and the photoconductivity threshold. It indicates that the same electron levels are absent for dark- and photoconductivity for the given poliimides. The temperature function of dark conductivity, the coincidence of $2E_t$ with E_{opt} and $E_{\lambda_{1/2}}$ gives us a basis to assume the character of photo- and dark conductivity for PPMI at elevated temperatures. Positive-charged acceptors for the photocurrent were determined by the sign of the photo-EMF (Dember effect). By using the thermo-EMF, it was established that holes are also acceptors of dark current. It follows, that PPMI are high-resistance semiconductors with dark- and photoconductivity, type r. The semiconducting properties of PPMI cannot be explained by double conjugated bonds throughout the system, since it has been noted (7) that for these polymers a conjugated chain is absent in sections, greater than the elementary unit. Intermolecular reaction between fragments of PPMI macromolecules are most likely the source of photo- and dark current acceptors. The coloring of PPMI is also due to this interreaction. Pyromellitic dianhydride is a strong electron acceptor and forms CPZ with many electron donor compounds (8,9). It can be assumed that similar electron acceptor properties will be found in the diimides of pyromellitic acid. It was shown that phthalic anhydride and phthalimide form CPZ with donor molecules. From the absorption spectra of CPZ, it follows that imides and anhydrides have approximately the same electron affinity. We discovered that pyromellitic acid diimide forms CPZ in a solution of DMCO with electron donors - eg. diphenylamine (max=445), carbazole (max=410), pyrene (max=410). The groups, forming diamide remains in PPMI, are capable of forming CPZ with external low molecular electron acceptors (quinone and polycyanocarbonic compounds) -ie. on the whole, they retained their electron donor character present in individual compounds (10). On the basis of this data, it can be assumed that there is a donor-acceptor interreaction, type CPZ, in the PPMI between electron acceptor promellitimide fragments and electron donor diamide remains in adjacent macromolecules, which accounts for the coloring of the poliimides and their electric

and photoelectric properties. A deepening in color was observed, as well as a decrease in the activation energy of dark conductivity and an increase in wavelength for the threshold and spectrum peaks of photoconductivity (Table) with a decrease in the ionization potential of the compounds  ,forming diamine remains in these polymers (for X=O, S, NH ionization potentials are equal to 8.09, 7.80, 7.14eV respectively {11}). A decrease in electric characteristics ($2E_t$, E_{opt}, $E_{\lambda_{1/2}}$) was observed, which was accompanied by an increase in conductivity and an increase in the concentration of unpaired electrons. Spectra parameters for conductivity are given below:

Polymer	PM	DOS	ODA
N·10⁻¹⁷, q⁻¹	0.28	0.80	3.30
g-Factor	2.0031	2.0030	2.0022
N, e	9	8	3

Although we cannot, as of yet, explain the bond between current carriers and PMC, it can be assumed that the formation of the latter and the creation of current carriers are the result of a donor-acceptor interreaction between corresponding fragments of macromolecules (as postulated by Blumenfeld' and Bendersky {12}). The creation of current carriers in PPMI, evidently, occurs with the transition of an electron, acted upon by light or heat, from the donor fragment to the adjacent promellitimide fragment, which is bonded to it in CPZ. If the migration or skipping theory in conductivity is correct, then an electron transfer or holes between identically charged and uncharged acceptor or donor fragments will occur on exposure to a field. A positive charge for dark and photo carriers is indicative of the mobility of holes. The formation of energy zones through donor-acceptor interreaction between macromolecules cannot be ruled out, and PPMI conductivity might be explained within the framework of this zone theory.

References

1. N.D. Malegina, T.A. Gordina, B.V. Kotov, V.S. Voishchev, A.N. Pravednikov, Vysokomolek. soed., B.14, 143, 1972.
2. V.S. Voishchev, B.I. Mikhant'ev, B.I. Sazhin, N.D. Malegina, B.V. Kotov, T.A. Gordina, Vysokomolek. soed., B.15, 361, 1973.
3. V.S. Voishchev, B.I. Mikhant'ev, B.I. Sazhin, V.P. Shuvaev, V.S. Yakubovich, Plast. massy., 1972, No. 8, 39.
4. V.S. Voishchev, B.I. Mikhant'ev, O.V. Voishcheva, N.D. Malegina, "Monomers and high-molecular weight compounds," Tr. VGU, ed. 2, Voronezh, 1972, p.95.
5. O.V. Kolninov, A.P. Terent'ev, Z.V. Zvonkova, E.G. Pukhadze, Report, AS USSR, 168, 1327, 1968.
6. O.V. Kolni nov, A.P. Terent'ev, Z.V. Zvonkova, E.G. Pikhadze, G.P. Talyzenkova, Report, AS USSR, 175, 639, 1967.
7. N.A. Adrova, M.I. Bessonov, L.A. Laiys, A.P. Rudakov, "Poliimides- a new type of heat resistant polymers," Nauka, 1968
8. O.V. Kolninov, V.M. Vozzhennikov, Z.V. Zvonkova, B.P. Glushkova, E.E. Shapiro,Report, AS USSR, 189, 353, 1969.
9. O.V. Kolninov, Z.V. Zvonkova, V.P. Glushkova, Zh. Fiz. Khimii, 43, 1498, 1969.
10. T.A. Gordina, B.V. Kotov, O.V. Kolninov, A.P. Pravednikov, Vysokomolek. soed., B.15, 378, 1973.
11. V.K. Potapov, Dissertation, 1972.
12. A.A. Blumenfeld', V.A. Bendersky, Zh. strukt. khimii, 4, 405,1963.