Translated from *Uspekhi Khimii*, 43, 1821-1843 (1974) U.D.C. 541.14; 547.212.4

Photoconductance of Organic Polymers

V.S.Myl'nikov

Photoelectric phenomena in organic polymers are analysed, attention being paid mainly to experimental and theoretical information on the mechanism of photoconduction. Macroscopic photoelectric properties are shown to have common features in polymers, inorganic semiconductors, and organic semiconductors of low molecular weight. A list of 218 references is included.

CONTENTS

I. Introduction 862
II. Polymers with triple bonds in the conjugated chain 862
III. Products of the thermal and radiation-thermal treatment of polymers 863
IV. Polymers with double bonds, heteroatoms, and heterocycles in the conjugated chain 864
V. Polymers with saturated main chains 866
VI. Mechanism of photoconduction in organic polymers 868

I. INTRODUCTION

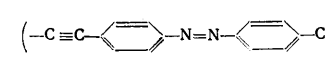
Isolated observations of an internal photoeffect in organic polymers at the beginning of the 1960s have now been replaced by regular and systematic investigations. Nevertheless, the short chapters in several monographs on organic semiconductors [1-10] and the single previous review [11] on the photoelectric properties of organic polymers have become out of date and do not give a full idea of the present-day state of this field of science. An attempt is now made to summarise information which has accumulated on the photoelectronics of organic polymers with the exception of organometallic and coordinated polymers, which have been considered in Ref. 12.

The investigation of photoelectric phenomena opens up great possibilities for studying the mechanism of the generation, drift, and recombination of current carriers, as well as for analysing the chemical and physical structure of organic polymers in the broadest sense. Use of a light beam ensures rapid transmission of information, uncoupling between individual channels of communication, high information capacity, and directional signals. In this connection organic polymers, with their specific physicochemical properties, are extremely promising materials for photosensitive cells with a wide range of uses in various technical devices. The Table sets out types of photosensitive organic polymers known at the present time.

II. POLYMERS WITH TRIPLE BONDS IN THE CONJUGATED CHAIN

Some of the first macromolecular compounds in which an internal photoeffect was detected [13] and studied systematically [11,13-28] were poly-ynes—compounds containing C≡C triple bonds in the conjugated chain—for which the main parameters determining the photoconductance and the photo-e.m.f. were examined. It was shown in particular that the dependence of the photocurrent i_{ph} on illuminance L is expressed by the formula $i_{ph} = \alpha L^n$, where $0.5 \leqslant n \leqslant 1$, [11,17-19] the photocurrent being proportional to the voltage raised to the power $1.2 < m < 1.7$. [17-19] In the large majority of poly-ynes the carriers of the photocurrent are positively charged [11,13,15-19], the kinetics of photoconduction is characterised by relaxation times from 10^{-5} s to a few minutes, and a hyperbolic law is obeyed [14].

Investigation and comparison of the photoconductance, photo-e.m.f., and absorption spectra [13,15-22] established that poly-ynes are intrinsic semiconductors, enabled the optical activation energies of photoconduction to be determined, and showed that the first stage in the generation of current carriers in polymers is the formation of excited molecular states or excitons. Preliminary exposure to ultraviolet radiation was found to activate the photoelectric sensitivity of poly-ynes [13,15]. Typical spectral curves of these compounds are shown in Fig. 1 for poly-*pp'*-diethylnylazobenzene



Optical activation energies of photoconduction determined from the photoconductance and photo-e.m.f. spectra agree with each other over the range 1.5–2.5 eV, and coincide with the edge of the fundamental absorption. This is evidence of the intrinsic character of conduction in poly-ynes. The optical activation energy of photoconduction is identical with the activation energy of electrical conduction [15], which indicates the common nature of these processes. The main photoconductivity maximum is situated, as in inorganic semiconductors, on the descending slope of the fundamental absorption, probably owing to the high rate of surface recombination.

With poly-ynes as example it was suggested that photoconduction in polymers should be regarded as a multistage process involving formation of an exciton and its subsequent dissociation on interaction with a defect or with another exciton [13,15-19]. Comparison of the absorption spectra of poly-ynes in solution and in the solid phase [16] indicates that intermolecular interaction is strengthened in the latter. The change in the photosensitivity of polymers produced by preliminary ultraviolet irradiation was explained by ionisation of the molecules followed by photopolymerisation [11,13,15] producing charged local centres, which is supported by the presence of a photoinduced electron spin resonance signal [17-20].

It is noteworthy in this connection that Wegner has obtained photoconducting polymers by exposing monomers containing conjugated triple bonds to ultraviolet radiation or high-energy electrons [28]. The photochemical modification of monomers with triple bonds and of polyacetylenes [29-31] is of interest for several recording systems. In all the cases examined the initial act of the photochemical reactions can be assumed to be the formation of free

electrons. This makes the investigation of photoelectric properties most promising for an understanding of the elementary acts in photochemical reactions. The discovery of photoconduction has enabled poly-ynes to be used for the preparation of electrophotographic layers [21,22]. Investigation of poly-ynes under electrophotographic conditions [24,25] has confirmed several effects and regularities observed under conditions of photoconduction and photo-e.m.f. (sign of carrier, spectral characteristics, activation of photosensitivity by ultraviolet radiation, etc.) and has enabled fresh information to be obtained on the properties of electrophotographic layers based on photosensitive polymers having triple bonds in the conjugated chain. It is noteworthy also that the photosensitivity of poly-ynes can be extended by dyes to longer wavelengths [18,19,34].

Photosemiconducting organic polymers.

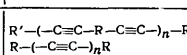
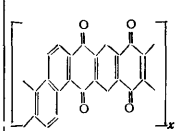
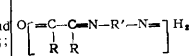
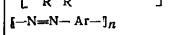
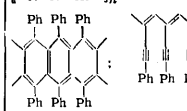
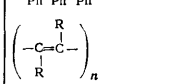
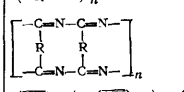
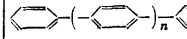
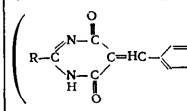
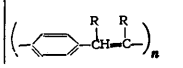
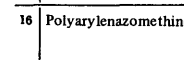
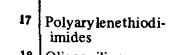
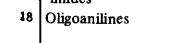
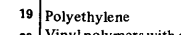
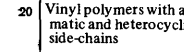
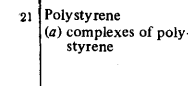
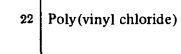
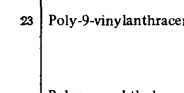
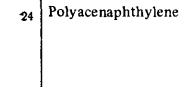
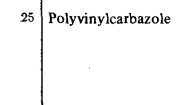
No.	Polymers	Structural formula of unit	Refs.
1	Poly-ynes (R = Alk, Ar, Hetaryl)		11; 13—28
2	Pyrolysis products from		
	(*a*) polyacrylonitrile		32, 33, 40, 41
	(*b*) regenerated cellulose		32, 33
	(*c*) phenol-formaldehyde resin		35, 188
	(*d*) poly(vinyl fluoride)		34
3	Products of photochemical treatment of vinylidene-vinyl chloride copolymer		44—46
4	Acenequinone radical polymers (PAQR)		36—39
5	Polyacrylonitrile and its complexes		40—43
6	Products of radiation-thermal modification of		
	(*a*) polyethylene		4, 52—55
	(*b*) poly(vinyl acetate)		53
	(*c*) polyimidazopyrrolones		56
7	Polymeric Schiff bases and polyazines: R = H, C_6H_5; R′ = *p*-C_6H_4		57—59, 68, 69
8	Polyazopolyarenes		60
9	Products of catalytic and thermal polymerisation of polydiphenyldiacetylene		62
10	Polyvinylenes		61, 63, 65—70, 75—77, 81—84, 100 121, 134
11	Polymeric acid diamides: R = CH_2, $CH_2.CH_2$, CH:CH		64
12	Polyphenylenes		61, 65, 66, 135
13	Polystyrylpyrimides		71
14	Polymers obtained in a discharge from monomers containing S, Se, N, and various metal atoms		72—74
15	Polyxylidenes		78, 79

Table (contd.)

No.	Polymers	Structural formula of unit	Refs.
16	Polyarylenazomethines		78, 79
17	Polyarylenethiodiimides		78, 79
18	Oligoanilines		80
19	Polyethylene		85—93, 95—100
20	Vinyl polymers with aromatic and heterocyclic side-chains		101, 102, 107—113, 117, 135, 180, 183, 186
21	Polystyrene		103—110, 114—116 135, 176
	(*a*) complexes of polystyrene		123, 131—133
22	Poly(vinyl chloride)		118, 184, 185
23	Poly-9-vinylanthracene		183
24	Polyacenaphthylene		181, 182
25	Polyvinylcarbazole		134—143, 165—173 179, 212—218
	(*a*) complexes		144—151, 162—164
	(*b*) with sensitisers		21, 24, 129, 134—139, 142—145, 151—161
	(*c*) with amorphous selenium		174—176
26	Polymers with added photosemiconductors		120—130, 177
27	Biopolymers		189—204

III. PRODUCTS OF THE THERMAL AND RADIATION-THERMAL TREATMENT OF POLYMERS

In the early stages thermal and radiation-thermal treatments were among the main methods of obtaining semiconducting organic polymer systems. Probably the first publications on the photoelectronics of these systems were brief communications by Mrosowski et al. on the possibility of using polyacrylonitrile and regenerated cellulose films pyrolysed at 800 °C as infrared detectors with sensitivity extending to 5 μm. [32,33] Pyropolymers based on poly(vinyl fluoride) and on a phenol–formaldehyde resin have since been proposed for infrared detectors [34,35]. Photoconduction has been observed in conjugated polymers based on acenequinone radical systems, polyacenes, Aniline Black, etc. by Pohl and his coworkers [36–39], who found that the *n*- and *p*-type conductivities of these compounds may vary from 10^3 to 10^{-13} ohm^{-1} cm^{-1}, and the mobilities of the current carriers from 10^{-6} to 100 cm^2 V^{-1} s^{-1}.

The photoconductance of the pyrolysis products of polyacrylonitrile was investigated in detail by Rozenshtein and his coworkers [40,41] who showed that, in the initial stage of thermolysis at 200–300 °C, conjugated segments of statistically unchanged lengths are formed in the polymer by cyclisation at nitrile groups. The kinetics of the growth of photoconductance during heat-treatment is

identical with that of the increase in the number of conjugated segments. Thus at this stage the increase in photoconductance is due solely to increase in the number of absorbing centres, not to a change in the mobility of the carriers. With rise in the treatment temperature the photoconductance spectra broaden and move to longer wavelengths with simultaneous increase in the absolute magnitude of the photoconductance and decrease in its relaxation time. Estimates of the upper limit of mobility based on the band model have shown that it increases from 0.01 to 40 $cm^2 V^{-1} s^{-1}$ with rise in the temperature of thermolysis from 200° to 500°C. The main result of work on the photoconductance of polyacrylonitrile must be regarded as the establishment that conjugated bonds are sufficient for the appearance of electronic conduction. Photoconduction may be observed in polyacrylonitrile also on complex formation with solvents, donor and acceptor molecules, as well as during its exposure to infrared radiation[42,43].

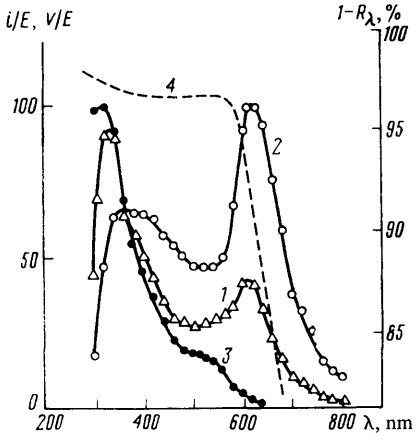


Figure 1. Spectra of poly-*pp'*-diethynylazobenzene[15,20]: 1) photoconductance; 2) as (1) after preliminary ultraviolet exposure (10 min); 3) photo-e.m.f. after preliminary ultraviolet exposure (10 min); 4) reflectance spectrum of unexposed polymer.

Exposure of a copolymer of vinylidene and vinyl chlorides to ultraviolet radiation results in the appearance of photosensitivity in the product[44-46]. The nature of the photoconductivity depends on the free radicals formed during irradiation, since conditions which induce and destroy the e.s.r. signal have similar effects on the photoconductance. Exposure to shorter wavelengths, e.g. X-rays, also produces an e.m.f. and induced conductance in polymeric materials[47-51].

Products of the radiation-thermal modification of polyethylene were investigated by Vannikov et al.[52,53]. Photocurrents of $\sim 10^{-12}$–10^{-14} amp were observed in the range 300–900 nm with light fluxes of 6 mW cm^{-2} and a multiplicity factor (ratio of photocurrent to dark current) exceeding 10. The activation energy of photoconduction ΔEph proved to be considerably smaller than the activation energy of electrical conductivity ΔEth, and decreased with increase in the photon energy on passing to more severely treated specimens. This decrease is probably due to the convergence of the conduction level of the polymer towards local levels determining the temperature dependence of the photoconductance. The photosensitivity under the same conditions of products based on poly(vinyl acetate) exceeds that of modified polyethylene some hundredfold[53].

Preliminary irradiation of high-pressure polyethylene with high-energy electrons led to a sharp increase in the photocurrent, whose principal region of sensitivity was situated in the near infrared[54,55]. Such irradiation had produced donor and acceptor traps, the formation of double bonds in the chains, and the cross-linking of separate macromolecules. A correlation probably exists between these double bonds and the traps of donor type. An energy diagram was given for the irradiated polyethylene with traps at levels 0.5, 1.1, and 1.7 eV below the conduction band. The activation energies for photoconduction and electrical conductivity are identical. The volt–ampere characteristics of the photocurrent indicate that space charges play an important part in establishing a photoresponse.

With polyimidazopyrrolones[56] at energies of ~15 mW cm^{-2} (polychromatic light) the observed current exceeded the dark current by a factor of 300. Maximum photosensitivity was reached after vulcanisation at 300°C for 24 h, when sensitivity was observed in the ultraviolet, visible, and near infrared regions with maxima at 610 and 550 nm. The photoconductance spectrum is displaced by about 35 nm to longer wavelengths compared with the optical absorption spectrum. Attempts to sensitise polymers by means of dyes were unsuccessful. The photocurrent obeys Ohm's law at field strengths of 10^2 to 10^5 V cm^{-1}. The observed thermal activation of the photocurrent suggests that generation of the carriers involves a complicated mechanism[56].

IV. POLYMERS WITH DOUBLE BONDS, HETEROATOMS, AND HETEROCYCLES IN THE CONJUGATED CHAIN

In this class of polymers photoconduction was first observed with certain polymeric Schiff bases and polyazines[57-59]. The lux–ampère dependence of the photocurrent was found to be below linear for all the specimens. The photocurrents increase exponentially with temperature and have activation energies of ~0.1–0.2 eV. The considerable polarisation phenomena made interpretation of the results difficult.

As the conjugated system in polyazopolyarenes[60] and their carbon analogues[61] becomes shorter, the photocurrent in the region of maximum absorption becomes smaller, the thermal activation energy of electrical conduction decreases, and the optical spectra undergo a hypsochromic shift. It is interesting that the activation energy of photoconduction increases with decrease in the photon energy. This has been linked with the molecular-weight distribution in the polymer, but requires detailed verification. In this case there may exist definite prospects for controlling and determining molecular-weight distributions in polymers by photoconduction methods. Variation of the activation energy of photoconduction with wavelength has been observed also in polydiphenyldiacetylenes[62], and is due to differences in the depth of the trapping levels involved in photoconduction. It has been shown for poly-ω-iodophenylacetylenes that the absorption in the range 400–1100 nm by various fractions is independent of the molecular weight of the polymer, the conjugated segments being shorter than the macromolecule[63]. The

photoconductance spectrum coincided with the form of the optical absorption spectrum. Photoelectric sensitivity was observed in a group of ladderlike polymers by Polak et al.[64] Photoconduction was suppressed by oxygen.

Photoconduction was established and studied in poly-*p*-phenylenes and several polyvinylenes by Beck[65,66]. The resistivity of specimens was $10-10^{15}$ ohm cm depending on the conditions of polymerisation and the oxygen content, and the activation energy of photoconduction varied from 0.025 to 0.96 eV. A tunnel mechanism of the passage of carriers through potential barriers was suggested for these polymers, and the mobility of the carriers was estimated as 0.6 $cm^2\ V^{-1}\ s^{-1}$.

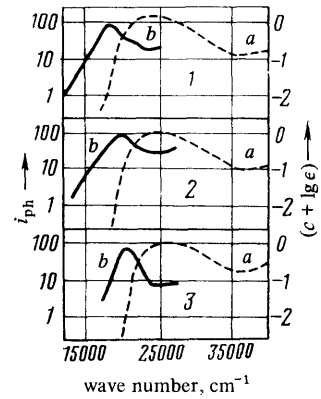
Grenishin, Cherkasov, and their coworkers[67-70] have been concerned with aspects of the relation between the structure and the photoelectric properties of polyenes (polyphenylacetylene, polydiphenylacetylene), acene structures (polydiphenylbutadiyne), structures with heteroatoms in the conjugated chain, and polymeric Schiff bases. Various methods have confirmed that the macromolecule is considerably larger than the average conjugated segment. The photosensitivity of polymeric Schiff bases[68] is independent of molecular weight over the range 200–1000, but increases tenfold on passing from amorphous to crystalline structures. Under electrophotographic conditions polymers containing carbon–nitrogen bonds exhibit photoconduction in the ultraviolet with quantum efficiencies of $(5-100)\times 10^{-6}$ el quantum^{-1},[69] which increase with the degree of delocalisation of electrons along the conjugated chain and with increased regularity of the structure. The photosensitivity of crystalline structures usually exceeds that of amorphous structures. It is generally concluded that segments of π-conjugation in polymers are no longer than those in low-molecular organic semiconductors, and hence that their electronic nature is the same. This evidently holds only for the stage of generation of photocarriers, which is regarded[70] as involving the formation and destruction of excitons as in poly-ynes.

The dependence of photoconductance on the chemical structure of the macromolecule has been studied on polystyrylpyrimidines[71]. With certain polymers and undispersed light the variation was about 10 000-fold. The photocurrent in a vacuum exceeds that in air almost hundredfold, a steady photoconductance is established within 1–2 min, and the range of photosensitivity is 400 to 900 nm. Maxima in the photoconductance spectra coincide with minima in the absorption spectra. No specific mechanism of photoconduction is suggested[71]. The variation in the absorption spectra of these compounds was ignored in the study of the effect of chemical structure on photoconductance, so that the results obtained by these workers must be approached with caution.

Photoconductance in the visible region has been observed with a multiplicity of several thousand in films obtained by the polymerisation in the glow discharge of monomers containing nitrogen, sulphur, selenium, and certain metal atoms[72,73]. A significant increase in photoconductance was observed on the addition of traces of iodine during polymerisation. The activation energy of photoconduction was 0.25 eV over the range 25–175°C, and 0.05 eV at lower temperatures. The first step in the generation of photocurrent carriers was regarded as the formation of excitons. Unfortunately, no information was given on the structure of the polymer films obtained in the discharge. They may contain several monomeric compounds which determine their properties. Photoemission data[74] indicate that films obtained in a discharge behave as large unsaturated molecules—not as polymers.

The action of dehydrogenating agents on poly(vinyl alcohol) yields a polymer having photosensitivity in the near infrared, electronic conductance with a concentration of charge carriers of 10^{16} cm^{-3}, and mobility 10^{-3} $cm^2\ V^{-1}\ s^{-1}$, both determined from the Hall constant[75]. Photosensitivity extending to 8 μm is observed in polyacetylene obtained by means of a Natta–Ziegler catalyst[76]. This polymer exhibited an identical thermal activation energy (0.27 eV) for electrical conduction and for photoconduction, which was regarded[76] as that needed for the transition of electrons from impurity levels to the conduction band. Prolonged exposure led to a decrease in photoconductance.

Indirect estimates have recently been supplemented by direct measurements of the mobilities of carriers in polymers. Thus values of $10^{-3}-10^{-5}$ $cm^2\ V^{-1}\ s^{-1}$ have been determined[77] for polydiphenylbutadiynes and poly(halogenophenylacetylenes). The results show the presence of many capture levels in these polymers.



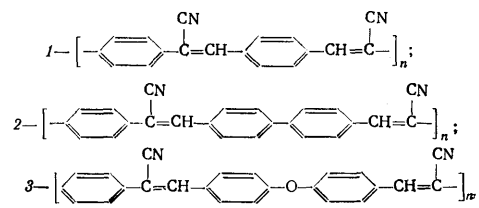


Figure 2. (*a*) Diffuse reflectance and (*b*) photoconductance spectra[79] of the polyxylidenes:

Extremely interesting work on the photoconduction of polyxylidenes[78,79] has established that the principal maxima are situated on the descending slope of the fundamental absorption, but an inverse correlation exists in the region of strong absorption (typical results are illustrated in Fig. 2). A correlation is shown between the optical activation energy of photoconduction, the activation energy of electrical conduction, and the theoretically calculated energies of $\pi-\pi^*$ transitions in isolated polymer molecules. Beyond four monomer units the optical absorption, fluorescence, and photocurrent spectra differ very little. This indicates that electron transitions in small conjugated segments are responsible for photophysical processes in polymers. Photoconduction was attributed to purely electron transitions, although a thermal activation energy of

of photoconduction was observed. Preliminary exposure to ultraviolet radiation leads to the appearance of a new maximum at longer wavelengths, which recalls the analogous phenomenon found with poly-ynes [10,13,20]. It is interesting that oxygen had opposite effects on the photoconductance at low and at high temperatures. The thermal activation energy of photoconduction lies between 0.03 and 0.2 eV depending on the surrounding atmosphere. In this work photoconduction was observed as far as the near infrared in polyarylenazomethines and polyarylenethiodiimides. All these polymers possess high resistances and may find application in electrophotography.

Photoelectric properties have been discovered and studied [80] in oligoanilines. The majority carriers in most compounds are positive holes. The optical activation energy of photoconduction is determined by shallow traps. The photoconductance spectra reproduce the absorption in the visible and the near infrared.

Finally, organic polymers containing conjugated bonds show a sharp increase in photosensitivity on reaction with electron-accepting compounds of low molecular weight [81-83]. This phenomenon is probably connected with the spectral sensitisation of low-molecular organic semiconductors by organic polymers with conjugated bonds [84].

V. POLYMERS WITH SATURATED MAIN CHAINS

Interest in photoelectric processes occurring in polymers with saturated main chains—in which conjugated bonds are either completely absent or are present in aromatic or heterocyclic side-chains—has recently increased sharply.

It has already been noted that certain types of polyethylene, after thermal treatment, develop photoelectric properties owing to the formation of segments with conjugated bonds [47,52,54,55]. Wintle et al. observed and investigated photoconduction in the untreated low-pressure polyethylene [85-88]. This work led to the most interesting conclusion, based on an examination of the absorption spectra of the polymer in solution and in the film, that the solid structure of the polymer was responsible for some absorption. The lack of correlation between photoconductance and absorption spectra indicated the impurity nature of the photoconduction. The mechanism of the production of free carriers in polyethylene was regarded as the distribution of charges in a series of irregularly connected barrier structures. It is noteworthy that van Roggen [94] detected barriers between single crystals of polyethylene that had been formed separately but were in contact. On application of an external field such structures function as current generators. Thermoluminescence data confirm the electronic–not ionic–nature of the conduction [95]. An exponential energy distribution of traps was shown [88] by the application of elementary band theory with the presence of short-range order to the charges trapped in the polymer chain. The conduction bands were very narrow, and mobility had a thermal activation energy of 0.1 eV. The photoconductance spectrum of polyethylene in the range 180–360 nm was determined by the corresponding structure in the optical absorption spectrum and the injection of electrons from the metal electrodes at their characteristic wavelength [90,91]. Photoelectric phenomena, governed mainly by contact-polarisation processes, were observed with polyethylene in the visible and in the near infrared from 0.6 to 1.7 μm. [89,91] Problems connected with the nature of photoelectric processes occurring in polyethylene and the role of the contacts have been discussed also in other papers [91-93,96,98,99]. The larger photocurrent observed with positive polarities on the leading electrode must be due to the photoinjection of holes, whose migration is determined by the Schottky type of emission [96]. The mobility of current carriers in polyethylene has been estimated as 10^{-5} cm^2 V^{-1} s^{-1} with activation energy ~0.25 eV, which is due to the thermal activation of charges out of traps or to a hopping mechanism of conduction [99]. Another study of the temperature dependence of photoconduction in polyethylene has appeared [97]. Papers on photoelectric processes in polyethylene are sometimes contradictory, especially with regard to the sign of the charge carriers, their mobility, and the interpretation of contact-polarisation phenomena.

Kryszewski et al. [100] observed photoconduction in the ultraviolet in polyethylene and several vinyl polymers; the multiplicity of the current reached hundredfold. It is significant that a larger photocurrent is observed in polymers having a higher degree of crystallinity; no clear relation was established between the photocurrent and chemical structure. The range of "saturated" polymers (i.e. containing no large conjugated fragments), in which photoelectric processes are observed has been extended considerably [101,102]. Photoelectrons emitted from the electrodes are assumed to govern conduction via traps. The current multiplicity reached 10^4 in individual commercial polymers (polyethylene, polypropylene, polystyrene, poly(ethylene terephthalate), polyvinylpyrrolidone, etc.). With several polymers (poly(vinyl fluoride), nylon-66, Viton, etc.) the density of the photocurrent attained 10^{-5} amp cm^{-2}, which is of interest for technical purposes. No special measures were undertaken to purify the commercial polymers, and most of the photoelectric processes in them are probably due to the presence of impurities and to contact phenomena.

Extremely interesting work has been done on the photoconductance of saturated organic polymers in the vacuum ultraviolet. Polystyrene shows an increase in photocurrent from 1400 to 500 Å. [103] Since the ionisation threshold of benzene molecules is 1330 Å, it may be assumed that the total ionisation energy is required to liberate an electron into the conduction band. The divergence between absorption and photoconductance spectra is interpreted here as the absence of an exciton stage in the generation of photocarriers. However, this disregards the effect of the thickness of specimens on the photoconductance spectrum. It is interesting that photocurrent and fluorescence increase simultaneously at wavelengths below 1400 Å. Detailed analyses have been made [104,105] of memory effects and of volt–ampère and lux–ampère relations in polystyrene. The volt–ampère characteristics are saturated at certain voltages, which depend on the light intensity. Oscillations of the photocurrent are observed in the same range. The mobility in amorphous polystyrene is 5×10^{-5} cm^2 V^{-1} s^{-1}; [106] the temperature dependence of charge transfer is small for jumps between molecular chains and strong for jumps between traps.

Aspects of the photoelectric properties of saturated polymers of type $[CH_2.CHR]_n$ have been dealt with in a series of papers by Grenishin, Cherkasov, et al. [107-113], who were the first to suggest using such systems to record images (electrography, photothermoplastic recording) in the spectral range 110–400 nm. Maximum photosensitivity under electrophotographic conditions was exhibited by layers of polyacrylonitrile, and minimum sensitivity by poly(vinyl chloride). In vinyl polymers the displacement (the product of the lifetime of the carriers and their

mobility) was 10^{-10} cm^2 V^{-1}, so that the carriers had a life of 10^{-7}–10^{-6} s, as mobilities in polymers of this type are 10^{-3}–10^{-4} cm^2 V^{-1} s^{-1}.[114] The quantum efficiency of the photoconductance of polystyrene in the range 110–160 nm is 2%. The optical absorption, reflectance, and photoconductance spectra indicated that the energy absorbed as exciton excitation is transmitted from "saturated" segments to aromatic side-chains, where dissociation with the formation of free carriers take place[108–112]. Analysis of the spectra of polystyrene showed that, the range up to 8 eV, absorption is determined by the properties of the monomer unit, but at higher energies by the electrons of the main chain. The absolute quantum efficiency of the photoeffect in the region of 6 eV was 10^{-4} el quantum^{-1}, which increased with the energy of the quantum to 0.4 el quantum^{-1} at 21 eV. Such high quantum efficiency may indicate the presence of a broad conduction band at a high level in the polymer. A partial criticism of the measurements on the photoconductance spectra of polystyrene suggests[115,116] that the application of a strong electric field in electrophotography may lead to distortion of the electron levels in the polymer and thereby to difficulties in distinguishing electrons involved in external and in internal photoeffects. These workers give a "band" model for polystyrene with an electron affinity of ~1.2 eV.

Vilesov et al.[117] have measured the photoelectric work functions of polyvinylcarbazole, poly(methyl methacrylate), polyvinylbutyral, and polystyrene as respectively 5.8, 5.9, 6.7, and 7.0 eV. Researches on the photoelectronics of "saturated" polymeric compounds include also investigations of pulsed photoconductance and of oscillating photocurrents in poly(vinyl chloride)[118], as well as the thermally stimulated conductance of poly(vinyl fluoride)[119].

Great interest is aroused by photosensitive systems comprising organic polymers into which have been introduced various photosensitive semiconductors such as zinc sulphide, cadmium sulphide, and zinc chloride, metal ions, dyes, and various doping agents[120–130].

Extremely promising investigations have been made during recent years on the photoelectric properties of charge-transfer complexes formed by two or more molecules. Such systems are distinguished by the appearance of a low-energy optical absorption band, by photosensitivity resulting from the transfer of charge, and by a sharp increase in conductance and photoconductance on complex formation. Papers have appeared on the photoelectronics of charge-transfer complexes of polystyrene[123,131–133]. One of the first and as yet one of the most actively investigated photosensitive polymer systems is polyvinylcarbazole[134–143] and its complexes[144–151,162–164], whose possible technical application in silverfree processes for recording images—electrophotography, photothermoplastic recording, etc.—is the primary reason for their interest[134–143]. References to the early patent literature on polyvinylcarbazole were given by Hoegl[135], together with data on the photoconductance of several polymers with heterocyclic and aromatic groups in the chain and of their complexes. The most photosensitive are probably complexes of polyvinylcarbazole with trinitrofluorene[138,145–149], electrophotographic layers of which are comparable in most of their characteristics with layers based on selenium[138]. The quantum efficiency in such layers reaches 0.15. Use of a laser source showed that, despite the extremely low mobility (5×10^{-8} cm^2 V^{-1} s^{-1}), the recombination rate constant is comparable with those for inorganic semiconductors. The nature, generation, and migration of current carriers in such systems have been discussed[148,149]. Photoconductance and a photoinduced electron spin resonance signal have been observed in complexes of polyvinylcarbazole with dinitrobenzene[150,151]. Hermann and Rembaum found that the Hall and Dember effects gave different signs for the carriers in iodine complexes of polyvinylcarbazole[162–164]. The photosensitivity spectra of such complexes cover the visible region with maxima in the ranges 400–500 and 700–800 nm. Pure polyvinylcarbazole possesses photoelectric sensitivity in the ultraviolet (Fig. 3). Sensitisation to the visible spectrum is therefore very important for technical purposes. A considerable number of papers have appeared on aspects of the spectral sensitisation of polyvinylcarbazole by dyes[129,134–139,142–145,151–159], and may form the basis of a separate review. The spectral sensitivity of polyvinylcarbazole can be extended by introducing other compounds, e.g. organocopper acetylides and poly-ynes[21,24,160,161].

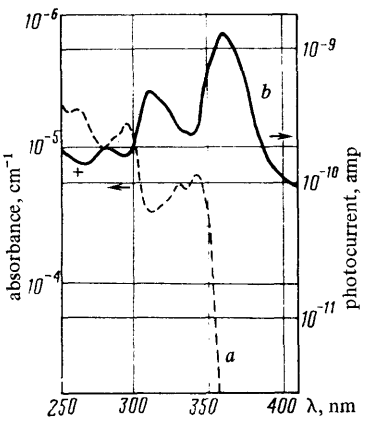


Figure 3. Spectra of polyvinylcarbazole[179]: *a*) absorption; *b*) photoconductance (with the illuminated electrode having positive polarity).

The mobility of holes in pure polyvinylcarbazole at room temperature is 0.001 cm^2 V^{-1} s^{-1} with a thermal activation energy of 0.12 eV.[165,166] The quantum efficiency of photogeneration is high (~0.1) and strongly dependent on the electric field[166,167]. The quenching of the photoluminescence of this polymer by an electric field is interesting in this connection[168]. The nature of the electrical conductivity of polyvinylcarbazole and the structure of the trapshave been examined[169,170].

Photoelectric phenomena have been studied at the contact between polyvinylcarbazole and metals[171–173]. The threshold photoemissions in the polymer were 1.28, 1.48, and 1.53 eV for gold, copper, and aluminium respectively. The ceiling of the valency band in polyvinylcarbazole is 6.1 ± 0.4 eV below the vacuum level. The development of a fine structure in the quantum efficiency spectrum is due to splitting of the electronic energy levels in the polymer by molecular vibrations. The width of the upper valency band in polyvinylcarbazole was estimated as < 0.11 eV. The generation of carriers is assumed[173] to involve intermediate formation of an exciton. Very interesting papers have appeared on the photoelectronics of polyvinylcarbazole at its interface with amorphous selenium[174–176]

and with cadmium sulphide and selenide[177]. Such heterogeneous systems may be expected to find application in several photosemiconducting devices.

A promising method for investigating the nature of photoelectric processes is the parallel study of the photoconductance and the luminescence of polymers. Examination of the latter has shown in particular that the energy absorbed by polyvinylaryls is not localised on side-chains, but is readily transmitted to neighbouring groups at distances of more than 1000 mean free paths[178,179].

Among other saturated polymers in which photoconduction has been observed and investigated are poly-1,3-diphenyl-5-*p*-vinylphenyl-2-pyrazoline[180], polyacenaphthylenes and their nitrile derivatives[181,182], poly-9-vinylanthracene[183], poly(vinyl chloride)[184,185], poly(pyrenylmethyl vinyl ether)[186], polytetrafluoroethylene exposed to X-rays[187], and an acenaphthene—formaldehyde resin[188]. All these polymers are high-resistance compounds of interest for electrophotography.

Finally, several papers have been published on the photoelectronics of biopolymers[189-024], the study of whose semiconducting properties is extremely promising for obtaining the energy parameters of these compounds and elucidating at a molecular level certain biophysical processes in living matter. The direct determination of the mobilities of charge carriers in proteins and nucleic acids gives values of 0.5–2 $cm^2 V^{-1} s^{-1}$.[197]

VI. MECHANISM OF PHOTOCONDUCTION IN ORGANIC POLYMERS

The experimental results surveyed in the preceding Sections show that the number of known photosemiconducting organic polymers is already quite large and is continuing to increase. They are of such varied types with respect to molecular (Table) and supermolecular structure that it is difficult to expect a single mechanism for the photoprocesses in all the compounds. Nevertheless, several quite general considerations will be discussed here.

The absolute photoelectric sensitivity (photoconductance, photo-e.m.f., etc.) of a polymeric compound should obviously be determined by two stages—(i) generation and recombination of free carriers and (ii) migration of the carriers through the polymer structure—a correct assessment of which would explain the following experimental principles, which have been established for most of the photoconducting polymers studied.

1. Photoelectric sensitivity is observed in polymers having conjugated bonds in the main chain in the macromolecule or in side groups.

2. The dependence of the photocurrent on the light intensity is below linear, and approaches linearity in isolated examples.

3. Ohm's law is satisfied for the photocurrent only up to field strengths of 100 V cm^{-1}.

4. Photoconduction is characterised by a wide range of relaxation times—from 10^{-5} s to several minutes.

5. The photoconductance and the electrical conductivity of polymers increase exponentially with rise in temperature, their activation energies being respectively 0.05–0.5 and 0.5–2.5 eV.

6. Mobilities of current carriers do not usually exceed 1 $cm^2 V^{-1} s^{-1}$.

7. Photoelectric effects are very sensitive to various external factors (preliminary exposure, effect of environment, illumination, etc.).

8. Photoelectric sensitivity is observed in the fundamental absorption band of the polymer, the main photoconductance maximum being located on the descending slope of the absorption spectrum.

A. Generation and Recombination of Carriers

One of the first papers on the photoconductance of organic polymers put forward the hypothesis, based on an analysis of the spectral dependence of photosensitivity in poly-ynes and on several experimental facts then known for low-molecular organic semiconductors, that the first step in the generation of current carriers in polymers is formation of an exciton, which migrates along the chain and between macromolecules[13]. The close similarity of the absorption spectra of polymers in solution and in the solid state[16,61,85] indicates that intermolecular interaction in solid polymers is quite small compared with orthodox inorganic photosemiconductors, and that the energy of the electromagnetic radiation is absorbed by individual molecules with formation of neutral excited states (excitons). The multistage generation of electron–hole pairs involving an exciton stage in the internal photoeffect in organic polymers has since received much additional confirmation[14-20,56,63,67-70,72,108-112,178,179] from data on photoconductance, luminescence, the effects of vapours and gases on photoconductance, etc. This view is now the most generally accepted. The exciton formed by the absorption of light migrates through the polymer matrix until it meets a defect or other excitons. Possible defects are disruptions in the chemical structure of the molecule, disruptions of crystallinity, cross-links between macromolecules, surfaces, etc. The number of defects in present-day polymers is so large that, in the majority of cases, these states govern the macroscopic properties. Nevertheless, direct measurement by luminescence methods of the diffusion constants of singlet and triplet excitons in polymers give extremely high values, of the order of 10^{-2}–10^{-6} $cm^2 s^{-1}$. Thus excitons are able during their existence to traverse 10–100 monomer units of the polymer. The capture of excitons by a defect or interaction with another exciton leads to its annihilation with formation of an electron–hole pair: carriers of one type remain attached to the defect, while those of the other type take part in conduction under the influence of the applied electric field, and the stage of charge transfer through the polymer structure is thus initiated.

It must be remembered that polymers have a considerable scatter of molecular weights, so that the excitons formed would also cover a certain range of energies. Such varied excitons, as well as factors influencing the drift of the carriers (barriers), may make a contribution to the usually small thermal activation energy of photoconduction (0.05–0.5 eV). This could explain in particular the wavelength dependence of this activation energy. However, there are data indicating that photoconductance is only weakly dependent on or completely independent of the molecular weight of the polymer[68,212]. However, the absence of significant bathochromic shifts in the fluorescence, absorption, and photoconductance spectra of polymers when the chain of conjugation exceeds a certain critical length[63,68,78,79,178,179] shows that the continuous chain of conjugation in organic polymers does not extend throughout the length of the macromolecule, but covers only a small number of monomer units (usually 2–7). This is supported by the observation of a hyperfine structure in the electron spin resonance spectra of certain

polyconjugated polymers[205]. It thus becomes clear why the introduction of various bridging groups which interrupt (or weaken) conjugation (those containing methylene, oxygen, nitrogen, or sulphur) does not lead to the disappearance of semiconducting properties.

Thus the optimum length of the system of conjugated bonds in polymers, that will lead to the specific photosemiconducting properties of these compounds, does not exceed a few units (usually < 10). This corresponds to the conjugated segments usually present in low-molecular compounds. Thus the first step in polymers, as in low-molecular organic semiconductors, is the formation of an exciton of a short segment of conjugated bonds. In this sense organic semiconductors of low and high molecular weights have the same electronic nature, as was to be expected. It now becomes clear why polymers with saturated main chains and aromatic side-chains can in principle be photosemiconductors, as is actually observed. The specific feature of polymeric compounds at this stage of generation of charge carriers is probably that the resulting exciton may possess a long lifetime owing to the rigidity of the polymer matrix, which ensures that excitons can migrate to great distances. The situation is analogous to the freezing of isolated molecules in solid solutions with the aim of lengthening the life of the excited state. The anisotropy of electrical properties would evidently be significant for polymers.

The concept of a "local activation effect", connecting the complex of physical (especially magnetic) and physicochemical properties of these compounds with their structural characteristics[206], may prove useful for discussing the photoconductance of polyconjugated polymeric systems obtained by thermal, radiation, etc. methods. Since photoconduction in "saturated" polymers has usually been studied on commercial specimens, it can reasonably be assumed that organic impurities having conjugated bonds were involved in the generation of current carriers. Direct ionisation of saturated bonds leading to the appearance of free carriers—and when irreversible to photodegradation of the polymer—is probably most feasible in the far and vacuum ultraviolet.

Recombination processes play a significant part in photosensitivity. They explain in particular the fact that maximum photoconductance in polymers is usually located on the descending slope of the fundamental absorption curve. Thus here, too, polymeric organic photosemiconductors behave similarly to the traditional inorganic semiconductors.

Preliminary exposure to ultraviolet radiation produces a change in photoelectric sensitivity both in organic polymeric[13–18,24,25,28,74,75] and in inorganic photosemiconductors (e.g. the formation of F-centres in crystals of alkali-metal halides, etc.[207,208]).

B. Migration of Carriers through the Polymer Matrix

Most organic polymers consist of alternating highly conducting regions (conjugated or condensed segments) and dielectric regions (disordered or amorphous structures). To effect photoconduction the electron–hole pair formed by breakdown of an exciton should drift in the applied electric field. The coincidence of the activation energy of electrical conductivity with the energy of the edge of the long-wavelength absorption and the red boundary of the photoeffect shows that the free carriers generated by the absorption of light are identical (even in the mechanism of drift) with those generated thermally.

A periodic chain of carbon atoms with the same number of hydrogen atoms attached would obviously have an electronic spectrum consisting of allowed and forbidden energy bands. Side groups replacing hydrogen atoms may act as impurities. Electropositive and electronegative substituents will correspond to acceptor and donor impurities. In contrast to covalent crystals, where impurity atoms may accept or donate one or more electrons, in the present case part of the electronic charge may be either fixed or released. Transfer of the complete charge may require several bonds acting in parallel. The numerous defects of various types present in the polymers at present available may also act as acceptor or donor impurities.

The mathematics of the band theory, which has been successfully used in studying the electronic properties of traditional inorganic semiconductors, is most fully developed at the present time. Most authors use this approach for the qualitative description of charge-transfer processes in organic polymers. When applied to macromolecular compounds, the band model supposes that current carriers move along generalised energy bands of π-electrons of the whole polymer. With decrease in the overlap of the π-electron wave functions the width of these bands diminishes, and in the limit they reduce to conduction energy levels, or to large effective masses of current carriers expressed in terms of the band model. This model implies strict periodicity in the structure of crystals and takes into account the potential for a real crystal in the effective mass of the current carriers. As already mentioned, however, most semiconducting polymers are heterogeneous or amorphous substances to a significant extent, and the application of a band model to polymers encounters certain difficulties. A possible way out may be to apply to such systems the theory of liquid and amorphous semiconductors, in which electronic properties are determined not by long-range but by short-range order[209,210]. These papers show that long-range order is sufficient but not necessary for the appearance of a band structure. Unfortunately, the main difficulties in discussing semiconducting processes in organic polymers in terms of a band model consist in the inability of this model to explain *quantitatively* several fundamental parameters observed experimentally. This applies primarily to the drift mobilities, which do not exceed a few units for most polymers, and in several cases are 10^{-6}–10^{-8} $cm^2\ V^{-1}\ s^{-1}$. The paradoxical situation arises in which the free path of the carriers becomes considerably shorter than the individual units in the molecule.

It is therefore most reasonable to adopt a hopping model of photoconduction for the majority of polymers. The free carriers formed by breakdown of an exciton probably remain localised in individual molecular segments or defects. Photoconduction is a consequence of a series of successive activated hops in the electric field. The activation energy of conductance then determines the probability of such hops[165,166]; the effective mobility or the effective concentration of current carriers should increase with rise in temperature. On theoretical grounds a hopping mechanism excludes the possibility that the Hall effect can be observed in systems where it operates. It is perhaps for this reason that attempts to observe the Hall effect on polymers have generally been unsuccessful.

The effect of light can in principle be regarded as lowering the potential barriers between separate macromolecules or regions of polyconjugation, which will increase the effective mobility of the carriers. Such a mechanism may perhaps be accepted for polymers in

which the concentrations of current carriers remain unchanged with rise in temperature. The appearance of non-equilibrium carriers exerting a polarising action may also lead to a lowering of barriers. The two processes (increase in carrier concentration and change in barrier height) may then occur simultaneously. Detailed analysis of the mechanism of conduction in semiconducting polymers is prevented by the insolubility or sparing solubility of most of the substances studied. As a consequence, comparative data are almost completely lacking on the absorption spectra of individual macromolecules (in solution) and on the absorption spectra and the photoeffect of polymers of uniform molecular weight in the condensed phase, so that no definite conclusions can be reached on collective interactions in polymeric semiconductors. It is therefore an urgent task to develop methods for synthesising soluble semiconducting polymers, which are necessary for assessing the role of intercrystalline and other defect interlayers in conduction processes, studied at present mainly on compressed pellets or powdered polymers.

A fruitful approach is to combine the concepts of hopping and band mechanisms for heterogeneous polymer structures. A band model can be applied to the motion of carriers within a conjugated segment, but transitions between such segments can be regarded as the activated surmounting of barriers. In fact, high-frequency measurements have shown that the activation energy within conjugated regions is almost zero[211]. With a large number of carriers present and sufficiently transparent barriers non-activated "percolation" of the former from one conjugated segment to another becomes possible.

---o0o---

The information on the photoelectric properties of polymers which has accumulated in a comparatively short time (10–15 years) is evidence of the rapid development of this field. However, future progress in scientific research and the widespread introduction of these materials into technology will encounter several obstacles. On a scientific level this is primarily the absence of clear ideas on the structure of many of the polymers investigated, which applies especially to products of the thermal, radiation, etc. treatment of polymers. Authors generally mention that the products obtained have a heterogeneous structure with regions of polyconjugation separated by certain barriers. Ideas on the size of the conjugated segments, crystallinity, packing, etc. are extremely vague. At the same time deductions are made on the relation between the chemical structure of a single macromolecule and the electrophysical properties of the whole polymer, which in such a situation is undoubtedly little justified. Analogous attempts to link semiconducting properties with specific chemical structures in the molecules of low-molecular organic semiconductors (dyes) have encountered substantial difficulties. It has not been shown that the decisive factor in establishing specific photosemiconducting properties in low-molecular organic compounds is the supermolecular structure, whereas the structure of the molecule (the presence of π-electrons) is responsible only for the fundamental possibility of such properties. This fully applies, in the opinion of the Reviewer, to polymeric compounds.

The situation is rather better with respect to polymers obtained by direct synthesis, for in most cases the chemical structure of the macromolecules is known exactly. Here too, however, the inadequacy of information on the significance of the physical structure of the products for their semiconducting properties is clearly felt. Little is known on the influence of defects and foreign impurities on the semiconducting properties of organic polymers. Yet it became possible to obtain inorganic semiconductors with specified properties only after they had begun to be thoroughly purified and then alloyed with definite impurities. For the solution of individual problems in semiconductor electronics the total content of impurities in inorganic semiconductors should not exceed 10^{-9}–10^{-10}%. For organic polymers in the best cases this ratio should be lower by factors of 10^{8}–10^{9}.

Thus it is not only important to seek powerful new semiconducting organic polymers but also urgently necessary to make a more detailed study of their specific physical structure as solids with simultaneous development of methods for their purification and for controlling impurities. Extremely promising work involves finding methods for and investigating mechanisms of the chemical and spectral sensitisation of photosensitivity in organic polymers by introducing molecules of sensitisers and of donor or acceptor agents.

The experimental and theoretical results surveyed in this Review show that organic polymers, hitherto regarded as exclusively insulating materials, possess several interesting photoelectric properties. The macroscopic development of these properties is analogous to those of inorganic and low-molecular organic photosemiconductors, which yet again emphasises the unitary nature of electronic processes in solids.

The voluminous literature on semiconducting organic polymers that has appeared during the past decade suggests that a new branch of the physics of solids—the physics of polymers having semiconducting properties—has recently been established. As with inorganic semiconductors, the study of photoelectric phenomena should become an independent section.

---o0o---

A group of Japanese workers have quite recently published a series of papers on the photoelectric properties of polyvinylcarbazole, its charge-transfer complexes, and its copolymers[213–217]. A book has appeared[218] on aspects of the application of organic polymers to electrophotography.

REFERENCES

1. V. A. Kargin (Editor), "Organicheskie Poluprovodniki (Organic Semiconductors), Nauka, Moscow, 1968.
2. J. E. Katon (Editor), "Organic Semiconducting Polymers", M. Dekker Inc., New York, 1968.
3. F. Gutman and L. Lyons, "Organic Semiconductors" (Translated into Russian), Mir, Moscow, 1970.
4. L. I. Boguslavskii and A. V. Vannikov, "Organicheskie Poluprovodniki i Biopolimery" (Organic Semiconductors and Biopolymers), Nauka, Moscow, 1968.
5. M. Kryszewski, "Polprzewodniki wielkocrasteczkowe", Warsaw, 1968.
6. A. A. Dulov and A. A. Slinkin, "Organicheskie Poluprovodniki" (Organic Semiconductors), Nauka, Moscow, 1970.

7. N. A. Bakh, A. V. Vannikov, and A. D. Grishina, "Elektroprovodnost' i Paramagnetizm Polimernykh Poluprovodnikov" (Electrical Conductivity and Paramagnetism of Polymeric Semiconductors), Nauka, Moscow, 1971.
8. Ya. M. Paushkin, T. P. Vishnyakova, A. F. Lunin, and S. A. Nizova, "Organicheskie Polimernye Poluprovodniki" (Polymeric Organic Semiconductors), Khimiya, Moscow, 1971.
9. B. I. Sazhin, "Elektricheskie Svoistva Polimerov" (Electrical Properties of Polymers), Khimiya, Moscow, 1970.
10. J. Okamoto and W. Brenner, "Organic Semiconductors" New York, 1964.
11. V. S. Myl'nikov, Uspekhi Khim., **37**, 78 (1968) [Russ. Chem. Rev., No. 1 (1968)].
12. Z. V. Zvonkova, Doctoral Thesis, Karpov Physicochemical Scientific Research Institute, Moscow, 1970.
13. V. S. Myl'nikov, A. M. Sladkov, Yu. P. Kudryavtsev, L. K. Luneva, V. V. Korshak, and A. N. Terenin, Dokl. Akad. Nauk SSSR, **144**, 840 (1962).
14. V. S. Myl'nikov, Dokl. Akad. Nauk SSSR, **148**, 620 (1963).
15. V. S. Myl'nikov, E. K. Putseiko, and A. N. Terenin, Dokl. Akad. Nauk SSSR, **149**, 897 (1963).
16. V. S. Myl'nikov, Dokl. Akad. Nauk SSSR, **157**, 1184 (1964).
17. V. S. Myl'nikov, Candidate's Thesis, Vavilov State Optical Institute, Leningrad, 1965.
18. V. S. Myl'nikov, in "Elementarnye Fotoprotsessy v Molekulakh" (Elementary Photoprocesses in Molecules), Nauka, Leningrad, 1966, pp. 417–433.
19. V. Mylnikov and A. Terenin, International Symposium on Macromolecular Chemistry, Prague, 1965, Preprint 128.
20. V. Mylnikov and A. Terenin, J. Polymer Sci., **C16**, 3655 (1968).
21. I. Sidaravichyus, F. A. Levina, G. I. Rybalko, V. S. Myl'nikov, A. M. Sladkov, Yu. P. Kudryavtsev, and L. Yu. Ukhin, Optiko-mekhan. Prom., **5**, 27 (1977).
22. F. A. Levina, V. S. Myl'nikov, G. I. Rybalko, I. B. Sidaravichyus, A. M. Sladkov, and A. N. Terenin, USSR P. 169 395 (1964); Byull. Izobr., No. 1 (1966).
23. I. L. Kotlyarevskii, A. B. Fisher, A. A. Dulov, A. A. Slinkin, and A. M. Rubinshtein, Vysokomol. Soed., **4**, 174 (1962).
24. I. B. Sidaravičius, Candidate's Thesis, Vavilov State Optical Institute, Leningrad, 1968.
25. I. Sidaravičius, J. Appl. Optics, Suppl. on Electrophotogr., 1969, p. 30.
26. A. M. Sladkov, Doctoral Thesis, Institute of Inorganic and Organoelementary Compounds, Moscow, 1967.
27. A. M. Sladkov and Yu. P. Kudryavtsev, Uspekhi Khim., **32**, 509 (1963) [Russ. Chem. Rev., No. 5 (1963)].
28. G. Wegner, Makromol. Chem., **154**, 35 (1972).
29. A. S. Hay, D. A. Bolon, K. R. Leimer, and R. F. Clark, J. Polymer Sci., **B8**, 97 (1970).
30. A. S. Hay, D. A. Bolon, and K. R. Leimer, J. Polymer Sci., **A-1**, 8, 1022 (1970).
31. W. Reid and R. H. Wessellorg, J. prakt. Chem., **12**, 306 (1961).
32. S. Mrosowski, E. D. McMichael, and E. A. Kmetko, Phys. Rev., **91**, 234 (1953).
33. B. D. McMichael, E. A. Kmetko, and S. Mrosowski, J. Opt. Soc. Amer., **44**, 26 (1954).
34. A. M. Glass, J. H. McFee, and J. G. Bergmann, J. Appl. Phys., **42**, 5219 (1971).
35. E. V. Suslov, V. V. Furin, E. S. Bakin, L. A. Pekal'n, and V. A. Filimonov, "Tezisy III Vsesoyuznogo Soveshchaniya po Organicheskim Poluprovodnikam" (Abstracts of the Third All-Union Conference on Organic Semiconductors), Kiev, 1971, p. 137.
36. H. A. Pohl and J. A. Bornmann, Z. Elektrochem., **65**, 649 (1961).
37. H. A. Pohl and D. A. Opp, J. Phys. Chem., **66**, 2121 (1962).
38. H. A. Pohl and E. H. Engelhardt, J. Phys. Chem., **66**, 2085 (1962).
39. H. A. Pohl, "Modern Aspects of the Vitreous State", London, 1962, Vol. 2, p. 72.
40. I. A. Drabkin, L. D. Rozenshtein, M. A. Geiderikh, and B. E. Davydov, Dokl. Akad. Nauk SSSR, **154**, 197 (1964).
41. I. A. Drabkin and L. D. Rozenshtein, Izv. Akad. Nauk SSSR, Ser. Khim., 1113 (1964).
42. E. A. Silin', D. E. Plumane, and A. V. Airapetyants, Elektrokhimiya, **2**, 608 (1966).
43. E. A. Silin' and D. E. Plumane, Elektrokhimiya, **2**, 732 (1966).
44. G. Oster, G. K. Oster, and M. Kryszewski, Nature, **191**, 164 (1961).
45. G. Oster, G. K. Oster, and M. Kryszewski, J. Polymer Sci., **57**, 937 (1962).
46. Nuova chim., **9**, 35 (1971).
47. J. E. Fowler and F. T. Farmer, Nature, **173**, 317 (1954).
48. P. H. Holt and D. T. King, Nature, **175**, 514 (1955).
49. V. D. Kuchin and A. K. Shastova, Vysokomol. Soed., **12**, 1863 (1962).
50. M. W. Partington, Nature, **174**, 136 (1954).
51. P. Hedvig, J. Polymer Sci., **A2**, 4097 (1964).
52. A. V. Vannikov, G. N. Demidova, L. D. Rozenshtein, and N. A. Bakh, Dokl. Akad. Nauk SSSR, **160**, 635 (1965).
53. I. A. Drabkin, Candidate's Thesis, Institute of Semiconductors of the USSR Academy of Sciences, Leningrad, 1967.
54. T. Tanaka, Jap. J. Appl. Phys., **5**, 974 (1966).
55. T. Tanaka and Y. Inuishi, Jap. J. Appl. Phys., **6**, 1371 (1967).
56. P. J. Reucroft, H. Scott, and F. L. Serafin, J. Polymer Sci., **C30**, 261 (1968).
57. B. E. Davydov, Yu. A. Popov, L. V. Prokof'eva, and L. D. Rozenshtein, Izv. Akad. Nauk SSSR, Ser. Khim., 759 (1963).
58. A. V. Topchiev, V. Korshak, Yu. A. Popov, and L. D. Rosenstein, J. Polymer Sci., **C4**, 1305 (1964).
59. B. E. Davydov, I. A. Drabkin, Yu. V. Korshak, and L. D. Rozenshtein, Izv. Akad. Nauk SSSR, Ser. Khim., 1664 (1963).
60. G. N. Demidova, R. N. Pirtskhalava, L. D. Rozenshtein, M. P. Terpugova, and I. L. Kotlyarevskii, Elektrokhimiya, **1**, 1145 (1965).
61. V. V. Sinitskii, G. F. Mechina, Yu. G. Kryazhev, and L. D. Rosenshtein, Izv. Akad. Nauk SSSR, Ser. Khim., 969 (1972).
62. B. E. Davydov, G. N. Demidova, F. M. Nasirov, R. N. Pirtskhalava, and L. D. Rozenshtein, Elektrokhimiya, **1**, 876 (1965).
63. I. A. Drabkin, M. I. Cherkashin, P. P. Kisilitsa, and A. A. Berlin, Elektrokhimiya, **4**, 1426 (1968).
64. L. S. Polak, A. F. Lunin, and A. M. Nechushkin, Izv. Vys. Ucheb. Zaved., Fiz., No. 3, 147 (1967).
65. F. Beck, Ber. Bunsenges. phys. Chem., **68**, 901 (1964).

66. F. Beck, Ber. Bunsenges. phys. Chem., **68**, 558 (1964).
67. Yu. A. Cherkasov, P. P. Kisilitsa, M. I. Cherkashin, and M. G. Chauser, "Tezisy III Vsesoyuznogo Soveshchaniya po Organicheskim Poluprovodnikam" (Abstracts of the Third All-Union Conference on Organic Semiconductors), Kiev, 1971, p. 59.
68. A. I. Myl'nikova, Yu. A. Cherkasov, and Yu. N. Polyakov, "Tezisy III Vsesoyuznogo Soveshchaniya po Organicheskim Poluprovodnikam" (Abstracts of the Third All-Union Conference on Organic Semiconductors), Kiev, 1971, p. 65.
69. Yu. A. Cherkasov, A. I. Myl'nikova, and Yu. N. Polyakov, Zhur. NiPFiK, **18**, 196 (1973).
70. S. G. Grenishin, Yu. A. Cherkasov, L. G. Kreitor, M. I. Cherkashin, and M. G. Chauser, "Trudy III Vsesoyuznoi Konferentsii po Besserebryanym Fotograficheskim Sistemam" (Proceedings of the Third All-Union Conference on Silver-free Photographic Systems), Kiev, 1972, p. 41.
71. R. Hirohashi, Y. Hishiki, and M. Haruta, Bull. Chem. Soc. Japan, **44**, 2573 (1971).
72. A. Bradley and J. P. Hammes, J. Electrochem. Soc., **110**, 543 (1963).
73. A. Bradley, Trans. Faraday Soc., **61**, 773 (1965).
74. P. L. Kronick, J. Appl. Phys., **39**, 5806 (1968).
75. L. Drechsell and P. Görlich, Infrared Phys., **3**, 229 (1963).
76. A. Matsui and K. Nakamura, Jap. J. Appl. Phys., **6**, 1468 (1967).
77. E. I. Merkulov, A. V. Vannikov, M. G. Chauser, A. N. Chigir', M. I. Cherkashin, N. A. Bakh, and A. A. Berlin, Izv. Akad. Nauk SSSR, Ser. Khim., 1399 (1969).
78. H. Hörhold and J. Opfermann, Makromol. Chem., **131**, 105 (1970).
79. H. Hörhold, Makromol. Chem., **12**, 41 (1972).
80. S. Neśpurek, Czech. J. Phys., **B23**, 368 (1973).
81. A. A. Berlin, I. A. Drabkin, L. D. Rozenshtein, M. I. Cherkashin, M. G. Chauser, and L. P. Kisilitsa, Izv. Akad. Nauk SSSR, Ser. Khim., 1339 (1967).
82. L. D. Rozenshtein, Doctoral Thesis, Institute of Semiconductors of the USSR Academy of Sciences, Leningrad, 1970.
83. V. V. Sinitskii, N. V. Kazanskaya, L. D. Rozenshtein, M. I. Cherkashin, and Yu. G. Kryazhev, Izv. Akad. Nauk SSSR, Ser. Khim., 1069 (1972).
84. I. Sidaravichyus, M. I. Cherkashin, B. G. Zadontsev, M. G. Chauser, A. I. Chigir', P. P. Kisilitsa, I. M. Shcherbakova, A. M. Meshkov, I. A. Akimov, and A. A. Berlin, Izv. Akad. Nauk SSSR, Ser. Khim., 527 (1971).
85. H. I. Wintle and A. Charlesby, Photochem. and Photobiol., **1**, 231 (1962).
86. H. I. Wintle, Photochem. and Photobiol., **3**, 249 (1964).
87. H. I. Wintle, Photochem. and Photobiol., **4**, 803 (1965).
88. H. I. Wintle, Photochem. and Photobiol., **6**, 683 (1967).
89. L. Vermeulen and H. I. Wintle, J. Polymer. Sci., A-2, **8**, 2187 (1970).
90. L. A. Vermeulen, H. I. Wintle, and D. A. Nikodemo, J. Polymer Sci., A-2, **9**, 543 (1971).
91. J. D. Comis and H. I. Wintle, J. Polymer Sci., A-2, **10**, 2259 (1972).
92. H. I. Wintle, J. Appl. Phys., **43**, 2927 (1972).
93. H. I. Wintle and C. M. Tibensky, J. Polymer Sci., A-2, **11**, 25 (1973).
94. A. van Roggen, Phys. Rev. Letters, **9**, 368 (1962).
95. A. Charlesby and R. H. Partridge, Proc. Roy. Soc., A283, 329 (1965).
96. T. Misutani, Y. Takai, and M. Jeda, Jap. J. Appl. Phys., **10**, 1465 (1971).
97. T. Mizutani, T. Ueno, Y. Takai, and M. Ieda, Jap. J. Appl. Phys., **12**, 757 (1973).
98. D. K. Das Gupta and M. E. Tindell, J. Phys., D5, 1368 (1972).
99. K. Hayashi, K. Yoshino, and Y. Jnuishi, Jap. J. Appl. Phys., **12**, 754 (1973).
100. M. Kryszewski, A. Shymanski, and A. Wlochowicz, J. Polymer Sci., **C16**, 3921 (1968).
101. A. E. Binks, A. G. Campbell, and A. Sharples, J. Polymer Sci., A-2, **8**, 529 (1970).
102. McGibbon, A. I. Rostron, and A. Sharples, J. Polymer Sci., A-2, **9**, 569 (1971).
103. M. Ofran, N. Oron, and A. Weinreb, J. Chem. Phys., **48**, 4805 (1968).
104. M. Ofran, N. Oron, and A. Weinreb, J. Chem. Phys., **49**, 960 (1968).
105. M. Ofran, N. Oron, and A. Weinreb, J. Chem. Phys., **50**, 3131 (1969).
106. E. H. Martin and J. Hirsch, J. Non-cryst. Solids., **4**, 133 (1970).
107. L. N. Vinokurova, S. G. Grenishin, and Yu. A. Cherkasov, "Tezisy III Naucho-tekhnicheskoi Konferentsii po Voprosam Elektrofotografii" (Abstracts of the Third Scientific and Technical Conference on Aspects of Electrophotography), Vilna, 1967, p. 29; "Trudy III Nauchno-tekhnicheskoi Konferentsii po Voprosam Elektrofotografii" (Proceedings of the Third Scientific and Technical Conference on Aspects of Electrophotography), Izd. Mintus, Vilna, 1972, p. 99.
108. L. N. Vinokurova, S. G. Grenishin, and Yu. A. Cherkasov, Zhur. NiPFiK, **4**, 299 (1968).
109. Yu. A. Cherkasov, L. N. Vinokurova, O. M. Sorokin, and V. A. Blank, Fiz. Tverd. Tela, **11**, 1977 (1969).
110. S. G. Grenishin, Yu. A. Cherkasov, L. V. Vinokurova, N. B. Zakharova, and A. I. Myl'nikova, International Congress of Photographic Science, Paper, E40, Moscow, 1970.
111. Yu. A. Cherkasov, L. N. Vinokurova, and P. P. Kisilitsa, Optika i Spektrosk., **34**, 805 (1973); see also Ref. 35, p. 37.
112. Yu. A. Cherkasov, L. N. Vinokurova, and P. P. Kisilitsa, Zhur. NiPFiK, **18**, 296 (1973).
113. Yu. A. Cherkasov, see Ref. 35, p. 34.
114. M. Kryszewski, A. Shymanski, and J. Swiatek, J. Polymer Sci., **C16**, 3915 (1968).
115. O. M. Sorokin and V. A. Blank, Fiz. Tverd. Tela, **11**, 2652 (1969).
116. O. M. Sorokin and V. A. Blank, Zhur. Prikl. Spektrosk, **9**, 827 (1968).
117. F. I. Vilesov, A. A. Zagrubskii, and D. A. Sukhov, Fiz. Tverd. Tela, **11**, 3409 (1969).
118. J. H. Ranicar and R. J. Fleming, J. Polymer Sci., A-2, **10**, 1321 (1972).
119. A. R. McChie, McGibbon, A. Sharples, and E. J. Stanley, Polymer., **13**, 371 (1972).
120. M. Sokolowski, and W. Szymanowski, Bull. Acad. polon. Sci., **8**, 191 (1960).
121. M. Kryszewski and M. Scorko, J. Polymer Sci., **C4**, 1401 (1963).
122. J. Kosiuczenko, Bull. Acad. polon. Sci., **21**, 91 (1973).
123. R. A. Wallace, J. Appl. Polymer Sci., **17**, 231 (1973).

124. M. J. Chockalingam, K. Nasakaja Rao, N. Rangarajan, and C. V. Suryanarayana, J. Phys. Appl. Phys., 5, 833 (1972).
125. M. Kosiwezenko and B. Klarner, Bull. Acad. polon Sci., 19, 671, 681 (1971).
126. H. Greig, Radio Corp. Amer. Rev., 23, 413 (1962).
127. W. Mehl, H. G. Grieg, and N. E. Wolf, Organic Crystal Symposium Abstracts, Ottawa, 1962.
128. W. Mehl and H. E. Wolf, J. Phys. and Chem. Solids, 25, 1221 (1964).
129. V. S. Myl'nikov, Zhur. Fiz. Khim., 42, 2168 (1968) [Russ. J. Phys. Chem., No. 9 (1968)].
130. W. C. Needler, J. Chem. Phys., 42, 2972 (1965).
131. M. Kryszewski, Acta Phys. Polonica, 26, 443 (1964).
132. A. Degorski and A. Tramer, Bull. Acad. polon, Sci., 15, 33 (1967).
133. W. Klopffer and H. Rabenhorst, J. Chem. Phys., 46, 1362 (1967).
134. C. Claus, Photogr. Sci. Eng., 7, 5 (1963).
135. H. Hoegl, J. Phys. Chem., 69, 755 (1965).
136. W. J. Wagner and E. L. Gasner, Photogr. Sci. Eng., 14, 205 (1970).
137. J. H. Dessauer and H. E. Clark, "Xerography and Related Processes", Focal Press, New York, 1965.
138. R. M. Schaffert, J. Res. Devel., 15, 75 (1971).
139. V. Uss, L. Nyun'ko, and I. Sidaravichyus, see Ref. 35, p. 46.
140. S. A. Zaidman, N. Ya. Filishov, D. I. Svirkin, and V. A. Kostylev, see Ref. 35, p. 69.
141. S. G. Grenishin and Yu. A. Cherkasov, see Ref. 35, p. 123.
142. K. Kriz, Photogr. Sci., 16, 58 (1972).
143. H. Yoneyma, M. Hirai, and H. Tamara, Bull. Chem. Soc. Japan, 45, 1932 (1972).
144. E. A. Lel and J. Weigl, International Conference on Photosensitisation in Solids, Abstracts D 4, Chicago, 1964.
145. M. Lardon, E. Lell-Doller, and J. W. Weigl, Mol. Cryst., 2, 241 (1967).
146. R. G. Hughes, Appl. Phys. Letters, 21, 196 (1972).
147. R. C. Hughes, J. Chem. Phys., 58, 2212 (1973).
148. P. J. Melz, J. Chem. Phys., 57, 1694 (1972).
149. W. D. Gill, J. Appl. Phys., 43, 5033 (1972).
150. G. Peister, M. Abkowitz, and D. J. Williams, J. Chem. Phys., 57, 2979 (1972).
151. D. J. Williams, M. Abkowitz, and G. Pfister, J. Amer. Chem. Soc., 94, 970 (1972).
152. H. Sato and M. Ikeda, J. Appl. Phys., 43, 4108 (1972).
153. H. Meier, W. Albrecht, and U. Tschirwitz, Photochem. and Photobiol., 16, 353 (1972).
154. H. Hoegl, G. Barchietto, and D. Tar, Photochem. and Photobiol., 16, 335 (1972).
155. S. Oka, T. Mori, S. Kusabayashi, A. Tanigucoi, Y. Yamamoto, N. Ishiguro, and H. Micawa, Electrophotography Japan, 5, 19 (1964).
156. Y. Hayashi, M. Curoda, and A. Inami, Bull. Chem. Soc. Japan, 39, 1660 (1966).
157. H. Okamoto, V. Hasegawa, S. Kusabayashi, and H. Mikawa, Bull. Chem. Soc. Japan, 41, 2563 (1968).
158. M. Ikeda, K. Morimoto, Y. Murakami, and H. Sato, Jap. J. Appl. Phys., 8, 759 (1969).
159. M. Ikeda, Y. Murakami, K. Morimoto, and H. Sato, Jap. J. Appl. Phys., 9, 931 (1970).
160. V. S. Myl'nikov, N. A. Agal'tsova, and A. M. Sladkov, Izv. Akad. Nauk SSSR, Ser. Khim., 203 (1972).
161. F. A. Levina, V. S. Myl'nikov, G. I. Rybalko, I. B. Sidaravichyus, A. M. Sladkov, and A. N. Terenin, see Ref. 22.
162. A. M. Hermann and A. Rembaum, J. Appl. Phys., 37, 3642 (1966).
163. A. M. Hermann and A. Rembaum, J. Polymer Sci., B5, 445 (1967).
164. A. M. Hermann and A. Rembaum, J. Polymer Sci., C17, 107 (1967).
165. A. Shymansky and M. M. Labes, J. Chem. Phys., 50, 3568 (1968).
166. D. M. Pai, J. Chem. Phys., 52, 2285 (1970).
167. J. Regensburger, Photochem. and Photobiol., 8, 429 (1968).
168. R. B. Comizzoli, Photochem. and Photobiol., 15, 399 (1972).
169. J. Patora, J. Piotrowski, M. Kryszewski, and A. Shymanski, J. Polymer Sci., B10, 28 (1972).
170. P. I. Reucroft, S. K. Ghosh, and D. Keerer, J. Polymer Sci., 10, 2305 (1973).
171. A. L. Lakatos and J. Mort, Phys. Rev. Letters, 21, 1444 (1968).
172. J. Mort and A. I. Lakatos, J. Non-cryst. Solids, 4, 117 (1970).
173. J. E. Carnes and R. J. Warter, Phys. Rev., B5, 1557 (1972).
174. J. Mort, Phys. Rev., B5, 3329 (1972).
175. J. Mort and P. Nielsen, Phys. Rev., B5, 3336 (1972).
176. J. Mort, I. Chen, R. L. Emerald, and J. H. Sharp, J. Appl. Phys., 43, 2285 (1972).
177. W. R. Salaneck, Appl. Phys. Letters, 22, 11 (1973).
178. G. I. Lashkov, Candidate's Thesis, Vavilov State Optical Institute, Leningrad, 1969.
179. H. Bauser and W. Klöppfer, Kolloid Z., 241, 1026 (1970).
180. K. Morimoto, Y. Hayashi, and A. Inami, Bull. Chem. Soc. Japan, 36, 1651 (1963).
181. A. Inami, K. Morimoto, and Y. Hayashi, Bull. Chem. Soc. Japan, 37, 842 (1964).
183. Y. Hayashi, M. Curoda, and A. Inami, Bull. Chem. Soc. Japan, 39, 1670 (1966).
183. M. Kazuhisa, I. Ishida, and A. Inami, J. Polymer Sci., A5, 1699 (1967).
184. A. Hersping and A. Oster, Kolloid Z., 226, 103 (1968).
185. T. Mizutani, Y. Takai, and M. Ieda, Jap. J. Appl. Phys., 11, 597 (1972).
186. S. Yoshimoto, K. Okamoto, H. Hirata, S. Kusabayashi, and H. Mikawa, Bull. Chem. Soc. Japan, 46, 358 (1973).
187. F. F. Kodzhespirov, F. I. Kolomoitsev, and L. Ya. Yakunin, Izv. Vys. Ucheb. Zaved., Fiz., No. 2, 142 (1964).
188. E. Port and J. Endszeewski, Bull. Acad. polon. Sci., Sér. Sci. math.-phys., 17, 319 (1969).
189. C. I. Liang and E. G. Scalco, Nature, 198, 86 (1963).
190. C. I. Liang and E. G. Scalco, J. Chem. Phys., 40, 919 (1964).
191. C. I. Liang, J. Chem. Phys., 43, 1835 (1965).
192. Yu. A. Vladimirov and K. N. Timofeev, Biofizika, 11, 33 (1966).
193. R. C. Nelson, J. Chem. Phys., 39, 112 (1963).
194. R. O. Becker and F. M. Brown, Nature, 206, 1325 (1965).
195. C. Forgace and C. Stein, J. Phys. Chem., 69, 4221 (1966).
196. H. C. Pant and B. Rosenberg, Photochem. and Photobiol., 14, 1 (1971).

197. E. M. Trukhan, Biofizika, **11**, 412 (1966).
198. H. T. Tien, Photochem. and Photobiol., **16**, 271 (1972).
199. E. Subertova, E. Silinsh, and V. Prosser, Czech. J. Phys., **B23**, 356 (1973).
200. V. S. Myl'nikov, Dokl. Akad. Nauk SSSR, **175**, 726 (1967).
201. E. K. Putseiko, Dokl. Akad. Nauk SSSR, **173**, 455 (1967).
202. E. K. Putseiko, Biofizika, **14**, 810 (1969).
203. V. V. Kompaniets and E. K. Putseiko, Biofizika, **18**, 550 (1973).
204. S. Suhai, J. Chem. Phys., **57**, 5599 (1972).
205. V. A. Benderskii, B. Ya. Kogan, V. F. Gachkovskii, and I. A. Shlyapnikov, "Karbotsepnye Polimery" (Carbon-chain Polymers), Izd. Akad. Nauk SSSR, Moscow, 1963.
206. A. A. Berlin, M. A. Geiderikh, B. E. Davydov, V. A. Kargin, G. P. Karpacheva, B. A. Krentsel', and G. V. Khutareva, "Khimiya Polisopryazhennykh Sistem" (Chemistry of Polyconjugated Systems), Khimiya, Moscow, 1972.
207. P. Görlich, Photoeffekte (Leipzig), **2**, 35 (1963).
208. A. V. Astraf'eva, F. F. Gavrilov, and V. L. Dvinyanikov, Izv. Vys. Ucheb. Zaved., Fiz., No. 8, 119 (1972).
209. A. F. Ioffe, "Fizika Poluprovodnikov" (Physics of Semiconductors), Izd. Akad. Nauk SSSR, Moscow and Leningrad, 1957.
210. A. I. Gubanov, "Kvantovo-elektronnaya Teoriya Amorfnykh Provodnikov" (Quantum-Electronic Theory of Amorphous Conductors), Izd. Akad. Nauk SSSR, Moscow and Leningrad, 1963.
211. L. I. Boguslavskii and L. S. Stil'bans, Vysokomol. Soed., **6**, 1802 (1964).
212. H. Epping, in "Current Problems in Electrophotography" (edited by W. F. Berg and H. Hauffe), Walter de Gruyter, Berlin, 1972, p. 215.
213. K. Okamoto, S. Kusabayashi, and H. Mikawa, Bull. Chem. Soc. Japan, **46**, 1948 (1973).
214. K. Okamoto, S. Kusabayashi, and H. Mikawa, Bull. Chem. Soc. Japan, **46**, 1953 (1973).
215. K. Okamoto, S. Kusabayashi, and K. Kosima, Bull. Chem. Soc. Japan, **46**, 2324 (1973).
216. K. Okamoto, K. Kato, K. Murao, S. Kusabayashi, and H. Mikawa, Bull. Chem. Soc. Japan, **46**, 2883 (1974).
217. K. Okamoto, S. Kusabayashi, and H. Mikawa, Bull. Chem. Soc. Japan, **46**, 2513 (1974).
218. W. F. Berg and K. Hauffe (Editors), "Current Problems in Electrophotography", Walter de Gruyter, Berlin and New York, 1972