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Electrophotographic Phenomena in Linear Polymers with Saturated and Conjugated Bonds

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The possibilities of varying the most important characteristics of organic polymers-electronic absorption spectra and the spectra of the quantum yield of the internal photoeffect, which to a large extent determine the limiting light sensitivity of silver-free and in the first place electrophotographic processes, are examined. The ways of increasing the quantum yield (electrophotographic sensitivity) by sensitising the internal photoeffect (spectral, structural, and injection) are analysed for linear polymers with saturated and conjugate bonds and polymeric charge-transfer complexes.
The nature of the phenomena underlying the photogeneration of free charge carriers in the class of substances under consideration is discussed. It is shown that the maximum electric fields under electrophotographic conditions ensure the attainment of the maximum quantum yield and correspondingly the maximum light sensitivity compared with other applications of organic semiconductors in photographic processes. The bibliography includes 97 references.

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I. INTRODUCTION

The development of methods for the optical recording of information and of means for its storage and processing as well as coherent optics requires the development of photographic processes with new characteristics, which are frequently in principle unobtainable in classical photochemical processes (treatment in a realistic time interval, the possibility of repeated recording of information, etc. as well as economic characteristics).

One of the new photophysical processes with the required characteristics is electrophotography (EP) based on the phenomenon of the photoeffect in electrically charged high-resistance films. Organic polymeric photoconductors are a promising class of materials for the formation of EP media. The combination of thermal stability and effective mechanical and other specific properties of polymers with those of photoconductors suggests that they will be widely used in the future as a basis for the creation of new photographic processes. Polymeric photoconductors possess technically important properties such as optical transparency, capacity for forming films, flexibility, and thermoplasticity and ensure that the appropriate layers can be readily manufactured on a technological scale at a low cost. The attractive possibility of synthesising photoconductors and particularly polymers with specified properties by methods of organic chemistry also initiated a vigorous development of research on these substances.

Studies on the possibility of manufacturing EP and other silver-free layers on the basis of polymeric photoconductors are being prosecuted at the present time in the USSR, the USA, Poland, Japan, German Federal Republic, and other countries and definite successes have been achieved in this field. Information about the applications and properties of organic photoconductors which are in principle suitable for EP processes can be found in a number of publications [1-6]. We shall only note that molecular organic compounds of a wide variety of classes, particularly anthracene and its substituted derivatives, pyrene, aryl-, diaryl-, and triaryl-amines, triaylmethane dyes and their leuco-bases, tetraarylmethanes, derivatives of furan and thiophen, pyrazolines, phthalocyanines, vinyl derivatives of heterocyclic compounds, organometallic compounds, polymeric compounds, polyacetylenes, polyvinylanthracene, polyacrylamide, modified poly(vinyl chloride), polyselenomethylene, and many others are used as light sensitive media. Numerous studies have been devoted to the use in electrophotography of poly-*N*-vinylcarbazole and other polymers containing in their structure the carbazole ring system, for example, polyallylcarbazole, polypropenylcarbazole, and poly-*N*-acryloylcarbazole and their derivatives, polymers and copolymers based on 1,4-divinylcarbazole, as well as polymers based on polyvinylcarbazole with amino-, nitro-, and halogeno-substituents introduced into the aromatic ring.

However, the problem of the relation between the magnitude and spectrum of the photosensitivity, on the one hand, and the structure of polymers, on the other, and of the limiting possibilities, particularly the limiting light sensitivity of photographic processes in organic polymers, still remains obscure. Nevertheless, interest in the study of these problems is associated not only with the possibility of improving considerably the parameters of the existing silver-free photographic processes but also with the possibility of discovering new promising principles for achieving such processes. The solution of these problems involves considerable difficulties, related not only to the usually low light sensitivity of polymeric structures but also to the extremely limited number of film-forming substances which can be used to create thin homogeneous photosensitive films.

In the present review an attempt is made to examine the relation between the quantum yield of the internal photoeffect and the structure of linear polymers and to investigate the possibility of increasing the quantum yield (EP-sensitivity) by sensitising the internal photoeffect (photoconductivity). Polymers with saturated and conjugated bonds and polymeric charge-transfer complexes

are examined from this standpoint and the possibility of their structural, injection, and spectral sensitisation is analysed. The aim of the present review is not to cover fully all the existing studies; furthermore, only those publications have been selected which contain data on the molecular and supermolecular structures.

II. STRUCTURAL CHARACTERISTICS AND ELECTRONIC SPECTRA OF LINEAR POLYMERS

In contrast to the π and σ electrons localised between two nuclei in saturated systems, the π electrons in compounds with a polyconjugation system belong to the entire conjugated section of the molecule as a whole, which leads to a different distribution of molecular energy levels. A relation between the position of the absorption band and the length of the polyene system has been established[7]. Theoretical examination of the spectra of infinite polymers with a conjugated system has shown that, when the length of the conjugated section $n_c \to \infty$, the distance between the ground and excited electronic levels $\Delta E \neq 0$.[8-10] In polyenes states with alternating single and double bonds are energetically more favourable. The absence of a bathochromic shift of the spectrum with increase of the degree of polymerisation n_p can therefore indicate both that $n_c \ll n_p$ and that initially the conjugated chain length n_c is the same as n_p when the degree of polymerisation increases, after which the bathochromic shift ceases[11]. According to estimates by different workers, ΔE is in the range 0.5–2.0 eV.

1. POLYMERS WITH SATURATED CARBON–CARBON BONDS IN THE MAIN CHAIN

The electronic absorption and reflection spectra in the vacuum ultraviolet region have been studied for a wide range of light-sensitive organic polymers with different molecular structures: vinyl polymers with functional groups; copolymers based on them; vinyl polymers containing aromatic substituents in a side chain; polymers with conjugated bonds in the main chain and with aromatic substituents; polymers containing aromatic rings as elements of the main chain[12-22].

The reflection spectra of vinyl polymers with different functional groups and copolymers based on them consist of a series of overlapping bands with individual maxima for each polymer (Fig. 1*a*). The spectrum of polyacrylonitrile (curve *1*) shows distinctly a band with a broad diffuse maximum at 115–140 nm and a maximum in the region of 100 nm. The reflection spectra of copolymers based on vinyl chloride consist of two bands with maxima near 90–100 nm and 145–155 nm. The reflection spectra of polymers containing benzene rings (Fig. 1*b*) consist of two bands: a short-wavelength band in the range 50–150 nm and a long-wavelength band in the range 150–250 nm. The band structure is specific to each polymer, but all the spectra show maxima near 195 and 90–100 nm. A decrease of temperature to 170 K (Fig. 1*a*) leads to the splitting of the maxima and a narrowing of the bands[13]. Thus maxima at 110, 137, 150, 184, and 210 nm are clearly seen for polyacrylonitrile; when the temperature is reduced, each of the two maxima of poly(vinyl chloride) is apparently split in two: the first has peaks at 97 and 110 nm and the second at 125 and 143 nm and a new maximum appears at 210 nm.

It has been shown[15] in relation to polystyrene that the reflection and absorption spectra in the vacuum ultraviolet region coincide. In relation to the absorption spectra of polymers with saturated bonds, the molecular exciton theory, based on the hypothesis that the bonds in the ground state do not interact and that there is a dipole–dipole interaction between them on excitation, predict a quasi-continuum[23]. The presence of absorption bands with distinct maxima in the spectra, the high photoconductivity quantum yield, reaching unity[24], and the correspondence between the positions of the absorption maxima in the spectral region associated with the ionisation of the monomeric unit [115 nm for poly(vinyl chloride) and 104 and 127 nm for polyacrylonitrile][25] makes it possible to relate the nature of the absorption by these polymers to the ionisation of the corresponding monomeric unit.

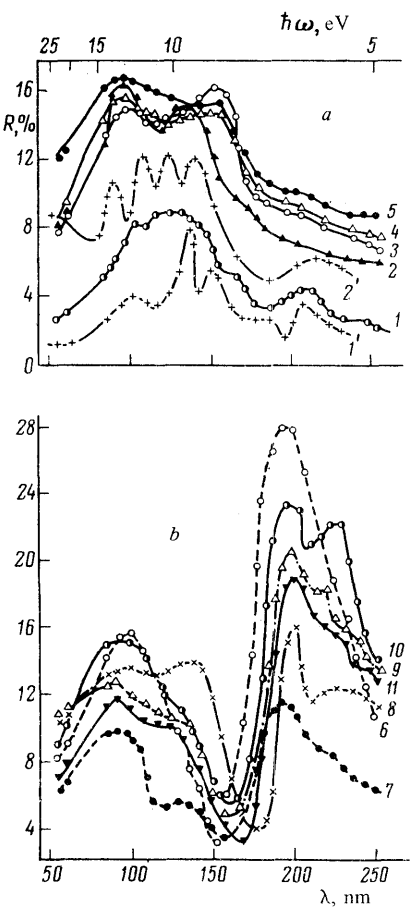


Figure 1. The reflection spectra of organic polymers with functional groups (*a*) and benzene rings (*b*)[13,14]: 1) polyacrylonitrile; 2) poly(vinyl chloride) [1^1) and 2^1) at 170 K]; vinyl chloride–vinylidene chloride copolymer; 4) vinyl chloride–vinyl acetate copolymer; 5) vinyl chloride–methacrylate copolymer; 6) polystyrene; 7) styrene–acrylonitrile copolymer; 8) styrene–2-ethylhexyl acrylate copolymer; 9) polytolane; 10) styrene–polytolane copolymer; 11) polycarbonate.

The presence in the reflection spectra of polymers containing benzene rings of maxima at 195 and 90–100 nm, characteristic of the excitation (195 nm) and ionisation (95 nm) [25] of benzene, suggest that the mechanism of light absorption by these polymers is determined by the properties of the benzene ring. Indeed the electron density of the monomer unit may shift towards the benzene ring in polymers containing benzene rings as elements of the main chain or side groups [26]. The nature of the absorption spectra of such polymers is then apparently determined by the properties of the benzene ring perturbed by the remaining atoms of the monomeric unit. In the 180–250 nm region of the spectrum (long-wavelength band), the π electrons of the benzene ring are responsible for the absorption [27], while in the short-wavelength region two excitation mechanisms probably operate: based on the π electrons and σ electrons of the bonds in the benzene ring. The latter process may be accompanied by the abstraction of a proton, since the energy of the C_6H_5–H δ bond is 12.6 eV (98 nm). [25]

The the absorption spectrum of vinyl polymers with different functional groups in the region 5–23.1 eV is determined by the properties of the monomeric unit and not the isolated bonds. The absorption spectra of polymers containing benzene rings either in the main chain or as side groups are determined by the properties of the benzene ring perturbed by the remaining atoms in the monomeric unit.

The low-temperature effect involving an "enhancement of the structure" of the absorption spectra [13] is associated with the vibrational excitation processes involving the molecules of a solid having a molecular structure. This effect can probably serve as direct proof of the significant role of vibrational excitation in making the structure of the energy spectra of photoelectrons less definite at 293 K for a number of aromatic crystals in the range 6–14.5 eV, which was observed by Zagrubskii and Vilesov [28]. The diffuse nature of the photoelectron spectra (this is also pointed out by Zagrubskii and Vilesov [28]) cannot serve as adequate evidence for the presence in the organic semiconductors of broad filled bands. Although Geacintov and Pope [29] showed by an analysis of literature data that the theory developed for indirect transitions in inorganic substances [30,31] is applicable to organic solids with a molecular structure (anthracene, tetracene), the idea of a continuous distribution of electrons with respect to energies in a molecular crystal is physically unjustified. The low mobility of charge carriers and the agreement between the absorption spectra of the crystal and the free molecule shows that the energy bands in these substances are very narrow [30–33].

On excitation with ultraviolet radiation, polymers of the vinyl series exhibit a universal luminescence in the range 70–400 nm, which depends strongly on the chemical structure, the degree of polymerisation, the degree of cross-linking of the polymer chains, the state of aggregation, and temperature, while on excitation with vacuum ultraviolet radiation the luminescence quantum yield depends on the wavelength of the exciting radiation [19,34–40].

2. POLYMERS WITH CONJUGATED CARBON–CARBON BONDS IN THE MAIN CHAIN

Since the chain in the polymer is non-planar and the degree of overlap of the π-electron orbitals depends on the angle of rotation about a single bond, it follows that, in all cases where the size of the conjugation block or the degree of conjugation in the block n_c are considered and compared with planar polyene reference systems, one is dealing with an effective conjugation where the size of the conjugation region n_c is not equal to the number of units in the block n_p. The effective conjugation is usually determined by comparing the positions of the maxima in the optical spectra of the polymer investigated and reference systems having a planar polyene chain [11].

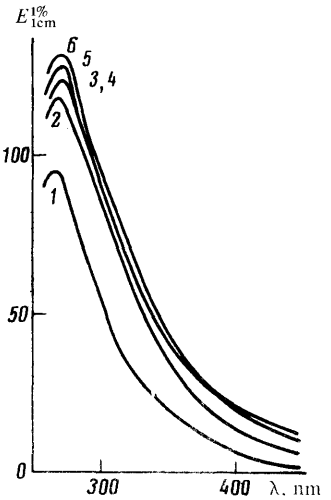


Figure 2. Absorption spectra of polychlorocyclopentene (solution in benzene) [11] for different molecular weights: 1) 450; 2) 1075; 3) 2450; 4) 3000; 5) 3660; 6) 4220 ($E^{1\%}_{1\,cm}$ optical density of 1% solutions for a cuvette 1 cm thick).

(a) Polymers with Double Bonds (Polyene Chain)

Poly-3-chlorocyclopent-1-ene (PCCP). An increase of the molecular weight (M) of the low-molecular-weight fraction entails an increase in the absorption intensity in the long-wavelength part of the spectrum [11] (Fig.2). The spectra of molecular fractions are very similar and the position of the maximum (270–274 nm) does not change from fraction to fraction and shows that small conjugated regions, embracing three units of the micromolecule (there are sections containing up to seven double bonds) predominate.

(b) Polymers with Aromatic Substituents [11]

Polyphenylacetylene, whose structure contains polymeric aromatic PPAT-150 conjugation blocks (phenylacetylene polymer obtained at 150°C) together with polyene units, has conjugation regions with an average length n_c, which is not the same as the length of the molecule and is smaller than the length of the lowest-molecular-weight fraction, i.e. $n_c \leq n_p = 8$. Treatment of PPAT-150 at 300°C (PPAT-150-300) results in an increase of absorption, although the molecular weight of the polymer

decreases (Fig. 3*a*). Comparison of the spectra of the PPAT-150 and PPAT-150-300 fractions leads to the conclusion that the average lengths of the conjugation regions in these polymers is smaller than the length of the units of the lowest-molecular-weight fraction, i.e. $n_C \leqslant 5$. Since the extinction coefficient ϵ is related to the optical density by the expression $\epsilon = E^{1\%}_{1\,cm} \times M/10$, where M is the molecular weight and $E^{1\%}_{1\,cm}$ the optical density of 1% solutions for an optical path length in the cuvette of 1 cm, it is found to be proportional to M of the fraction at the same wavelengths and the number of absorbing centres increases with increase of M of the polymer. The dimensions of the absorbing centre incorporate a region smaller than the length of the polymer chain.

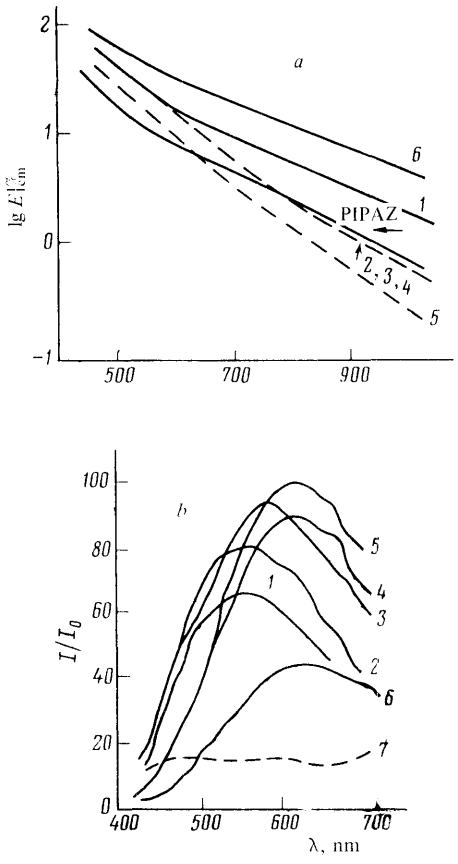


Figure 3. Absorption (*a*) and luminescence (*b*) spectra of polyphenylacetylene [11]: *a*) [1) PPAT-150 (790); 1′) PPAT-150 (1370); 2) PPAT-150-300 (500), PPAZ (2900); 3′) PPAZ-760; 4) PPAT-300 (760); 5) PPAT-400 (300); 6) PPAT-150-400 (650)]; *b*) [1) PPAT-150 (1060); 2) PPAT-150 (1590); 3) PPAT-150 (800); 4) PPAT-150 (1310); 5) PPAT-150 (1340); 6) PPAT-150 (1510); 7) PPAT-150 (2160); 8) PPAT-150 (1200); 9) PPAZ (1020); 10) PPAZ (2900); 11) PPAZ (5300); 12) PPAZ (7600)]. Here and henceforth the numbers in round brackets are the molecular weights M and the numbers in front of the brackets represent the polymerisation or heat treatment temperature (°C). The luminescence spectra are given in relative equienergetic units (I/I_0).

The average length of the PPAZ conjugation region [phenylacetylene polymer obtained in the presence of the $(C_2H_5)_3AlTiCl_3$ catalyst] proves to be greater than for PPAT-150 and PPAT-150-300, but smaller than for PPAT-300. Despite the fact that the average number of polymer units in PPAZ is 70–80, the average length of the conjugation region does not exceed the length of the conjugation region in PPAT-300, i.e. $n_C < 8$. Since the absorption of PPAZ is weaker than that of PPAT-300, it is difficult to suppose that the absence of a bathochromic shift of the PPAZ absorption spectrum is associated with the attainment of the equality $n_C - n_p$. PPAC apparently consists of individual short conjugation regions [11]. The spectra of the PPAT-150-400 fractions have a different form. Here there is a distinct increase of absorption intensity in the long-wavelength region with increase of M of the polymer. The increase of absorption intensity in the region of long wavelengths with increase of the temperature of the synthesis or heat treatment corresponds to the formation of longer conjugation regions. At the same time the average length of the polymer chain decreases. The average length of the conjugation region in PPAT-150-400 now includes the entire macromolecule. The value of M shows that PPAT-150-400 cannot have a value of n_C greater than 3–7. Comparison with the spectra of polyenes shows that the average length of the conjugation region does not exceed 5–6 for PPAT and 7–8 for PPAZ.

The luminescence spectra of PPAT [11] consist of a family of similar curves whose maxima are located at similar wavelengths (580–660 nm) with certain differences in the structure and intensity of the lines (Fig. 3*b*). It had been established earlier that similar changes in the spectra, characterised by a redistribution of the intensities in their fine structure, are observed when M (chain length) and polymer structure are altered, being particularly pronounced for chain molecules with a conjugation system [41]. Hence it follows that identical, within certain limits, positions of the maxima in the luminescence spectra are characterised by the same effective conjugation n_C. Assuming that the positions of the maxima in the luminescence spectra of PPAT and polyene chains are the same, one can conclude that the PPAT-150 fractions contain conjugation blocks with $n_C = 5$–6. This follows from a comparison of the PPAT spectra with the spectra of diphenylpolyenes both in solution and in the solid state. The average position of the maximum in the luminescence spectra of the PPAT-150 fractions is at ~620 nm, i.e. in the region between the maxima of diphenylhexatriene (530 nm) and diphenyloctatetraene (670 nm). One can therefore suppose that the conjugated chains of the PPAT-150 fraction have luminescence characteristics identical with those of a compound having intermediate properties.

The fact that the spectra of different fractions have different structures with some variation in the position of the maximum (which should not happen if the continuous conjugation sections contain identical numbers of units) confirms that the fractions contain in their chains different combinations consisting mainly of blocks with $n_C = 5$ and 6. The luminescence spectra of such polymer chains, in which regions with the larger value of n_C predominate in the solid state, should exhibit a lower intensity and the band maxima should be displaced towards longer wavelengths as a result of a redistribution of intensities in the individual bands of the fine structure of the spectrum. When regions with the lower value of n_C predominate, the opposite rearrangement of the structure of the absorption spectrum should occur. The statistical contribution of

regions with $n_C < 6$ and $n_C < 5$ is very insignificant: they are not observed in the spectra. Conjugation regions with $n_C > 6$ cannot actually be manifested in the spectrum owing to the low intensity of their luminescence in the solid polymer and the small number of such regions. On the other hand, regions with $n_C = 4$, the luminescence intensity of which in the solid state exceeds that observed for the conjugated regions with $n_C = 5$ by a factor of ~10, should appreciably increase the luminescence intensity of the spectrum in the region of 440 nm even when their content in the chain is low. However, the luminescence of the polymer in this region is insignificant, so that one may conclude that the number of conjugate regions with $n_C = 4$ in the overall balance is extremely small. The spectra of the PPAT fractions 6 and 8 (Fig. 3) characterise chains made up of individual conjugated regions with $n_C = 5$ and 6. In terms of the relative luminescence yields of these regions, their ratio in the above fractions can be estimated as 1 : 7.

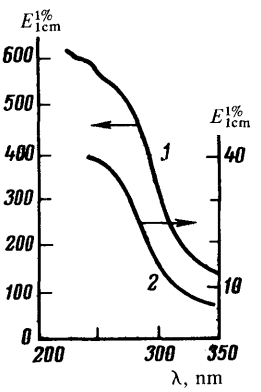


Figure 4. Absorption spectra of polymethylethynylpyridine (curve *1*) and polyphenylacetylene (curve *2*).[11]

With increase of M, the maximum in the luminescence spectra of PPAZ is steadily displaced towards longer wavelengths and the intensity falls sharply[11,41,42]. This change in the spectrum shows that M and the conjugation increase in parallel. PPAZ differs markedly from PPAT by a higher molecular weight M and a more extensive continuous conjugation. Analysis of the spectra shows that the chains in all the fractions of this polymer consist of different combinations of regions with $n_C = 6$–9. The markedly diffuse nature of the maxima in the spectra of all the fractions indicates a broad statistical distribution in terms of the extent of conjugation. All the fractions should therefore contain the regions with all the continuous conjugations enumerated above in the appropriate proportions. The PPAZ fraction 5 contains predominantly regions with $n_C = 6$ and 7, conjugation regions with $n_C = 7$ predominate in the PPAZ fraction 6, while regions with $n_C = 8$ predominate in the PPAZ fraction 8.

Polymethylethynylpyridine (PMEP) [11] does not differ from PPAT as regards the principle underlying the structure of the macrochain and the earlier conclusions are valid also for it. The electronic spectra of PMEP and PPAT (Fig. 4) do not show significant differences, particularly in the region of 300 nm, and consist of curves without appreciable maxima, which decrease in the direction of longer wavelengths; the absorption in the visible region is insignificant. It appears that the continuous conjugation extends to regions with $n_C = 3$–5.

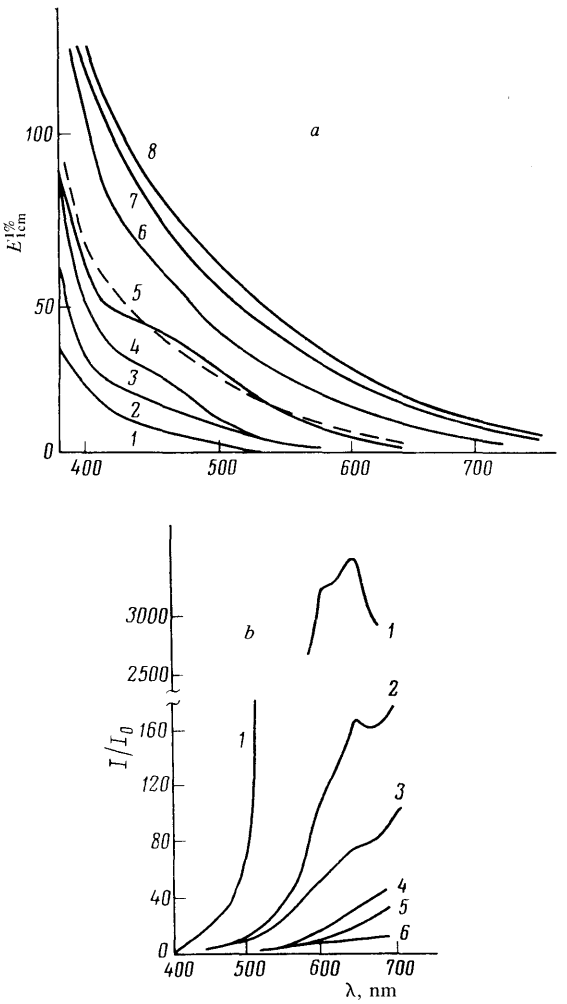


Figure 5. Absorptions (*a*) and luminescence (*b*) spectra of polydiphenylacetylene [11]: *a*) [1) 400 (406); 2) 300 (675); 3) 300 (830); 4) 300 (920); 5) 350 (1060); 6) 400 (860); 7) 400 (950); 8) 400 (660)]; *b*) [1) 300 (850); 2) 300 (850); 3) 350 (1060); 4) 400 (660); 5) 400 (930); 6) 400 (1200)].

(c) Polymers with Two Aromatic Substituents

Polydiphenylacetylene (PDPA) consists of a linear polymer whose structure contains a system of conjugated bonds and aromatic side groups which stabilise the main polyene chain of the macromolecule[43]; the end groups consist of hydrogen atoms. An increase of M induces a bathochromic shift of the absorption band (Fig. 5*a*), i.e. the length of the conjugation region is comparable to the

length of the macromolecular chain. However, an increase of polymerisation temperature causes an even greater shift for the same value of M (curves *6* and *9*), which is apparently due to the inclusion of benzene rings in the conjugation chain.

The luminescence spectra of PDPA [11,44] (Fig. 5*b*) are analogous to those of PPAT and PPAZ. The position of the PDPA-300 (polymer obtained at 300°C) luminescence maximum shows that these polymers are characterised by $n_C = 6$ with some proportion of regions with $n_C = 7$ and an insignificant content of regions with $n_C = 5$. Since PDPA-300-6 and PDPA-300-10 (polymerisation times 6 and 10 h respectively) have molecular weights of 850 and 930 respectively, while $M = 180$ for the monomeric unit, the PDPA-300-6 chains are continuously conjugated over the entire length of the system; the benzene rings are then included in the conjugation chain. The high intensity of the luminescence of PDPA-300-6 is comparable to the intensity of the luminescence of special technical phosphors.

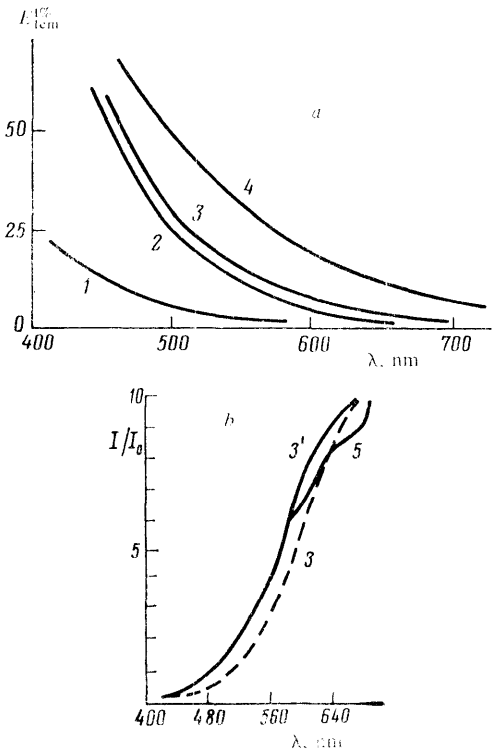


Figure 6. Absorption (*a*) and luminescence (*b*) spectra of polydiphenylbutadiyne [11]: *a*) [1) (1080); 2) (1450); 3) (3500); 4) product of the heat treatment of the non-fractionated polymer at 400°C ($M = 2100$)]; *b*) [3) (940); 3′) (2000); 5) (2120)].

(d) Polymers with a Binary Conjugation System (Acene Structures) [11,44]

Polydiphenylbutadiyne (PDPB). A change in M by a factor greater than 2 (from 1450 to 3500) does not entail a significant change in the spectrum (Fig. 6*a*). On this basis, it is suggested that the degree of continuous conjugation n_C in PDPB is constant and does not agree with the length of the macromolecule. Heat treatment of the polymer at 400°C is accompanied by an appreciable increase of absorption intensity in the long-wavelength region of the spectrum. The increase of the conjugation block on heat treatment can be associated primarily with the additional cyclisation of the polyene fragments. Furthermore, heat treatment promotes a coplanar arrangement of sections of the macromolecule which had been rotated in different ways prior to this and also a decrease of strain within the cyclic regions of the chain and the inclusion in the conjugation chain of some of the benzene rings in the side groups. However, within certain limits the positions of the bands in the luminescence spectra characterise the same values $n_C = 6$ and 7 (Fig. 6*b*).

Optically homogeneous films can be obtained from PDPB by vacuum vaporisation [44]. In a vacuum of 10^{-5}–10^{-6} mmHg at a melt temperature of 500°C, a rate of deposition of the layer not exceeding 0.05 μm min^{-1}, and a temperature of the surface (support) on which the vapour is condensed up to 450°C, optically homogeneous layers are obtained, greatly exceeding in terms of this parameter layers prepared by casting from solution [44]. Vacuum sputtering increases appreciably the optical density of the layer compared with the layers obtained from solution (Fig. 7). A determination of the average molecular weight of the PPAZ decomposition products [15] suggests that the PDPB molecule is broken up during vacuum sputtering at the weakest sites in the chain into blocks consisting of several units.

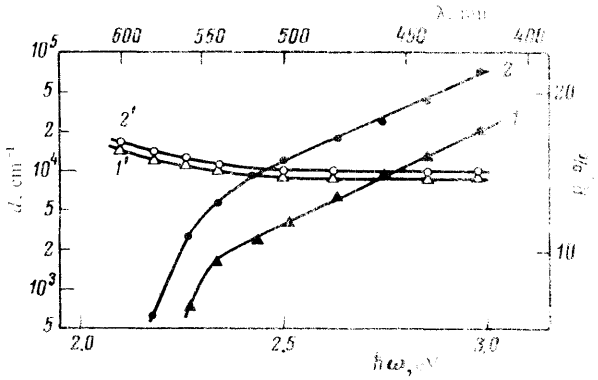


Figure 7. Absorption (curves *1* and *2*) and reflection (curves *1′* and *2′*) spectra of polydiphenylbutadiyne films obtained from solution (curves *1* and *1′*) and by evaporation in a high vacuum (curves *2* and *2′*). [44]

Poly-β-iodophenylacetylene. β-Iodophenylacetylene polymers obtained by thermal polymerisation (PIPAT) and polymerisation in the presence of Ziegler–Natta catalysts (PIPAZ) exhibit an appreciable absorption in the visible and ultraviolet regions characteristic of conjugated systems [11] (Fig. 8*a*). In the red and near infrared regions the absorption of PIPAT is stronger than that of PIPAZ. In the blue-violet region their absorptions are approximately the same. There is no structure whatever in the spectrum and the latter is markedly diffuse.

The continuous conjugation extends over regions which are small compared with the length of the molecule. The low value of $E^{1\%}_{1\,cm}$ shows that the fraction of molecules with long conjugation regions is small.

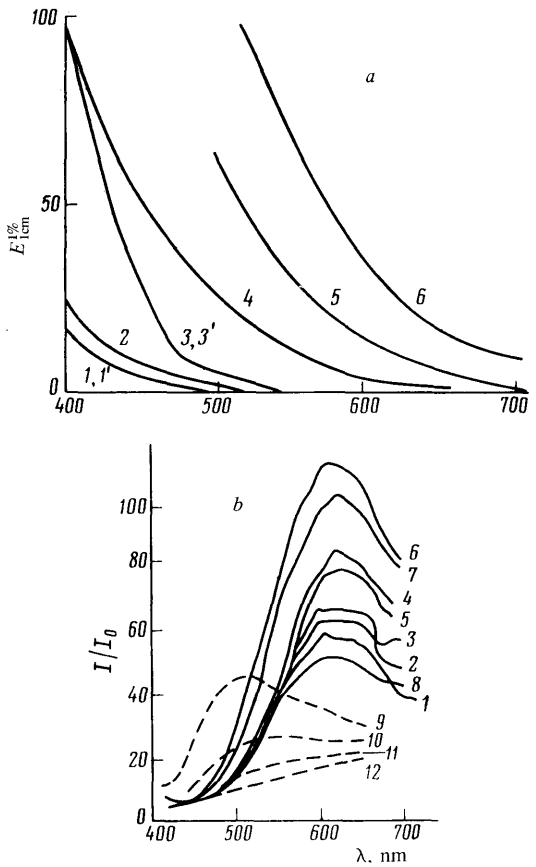


Figure 8. Absorption (*a*) and luminescence (*b*) spectra of polyiodophenylacetylene[11]: 1) (1300); 2) (1000); 3) (1770); 4) (2200); 5) (870); 6) (2400); 7) iodophenylacetylene (IPA) dimer with M = 456, PIPAZ (1680).

Bearing in mind that the different substitutions of side groups by other groups in simple carbon–carbon chains leads to an alteration of the structure of the spectra the extent of which is much smaller than the change in the position of the maximum caused by the difference in the degree of continuous conjugation in the chain[41], and despite the possible influence of iodine, one can estimate approximately the structure of the chains. Thus fractions *1* and *2* contain blocks with n_C = 6 and n_C = 6 and 7 respectively; fraction *3* contains regions with n_C = 7 and to a small extent n_C = 6; fractions *4* and *6* consist predominantly of regions with n_C = 7 and 8. Comparison of the molecular weights and the sizes of the conjugation region shows that in this instance continuous conjugation does not apparently embrace the entire macromolecule and individual conjugation blocks exist.

3. POLYMERS WITH CONJUGATED CARBON–NITROGEN BONDS IN THE MAIN CHAIN

Polymers with conjugated carbon–nitrogen multiple bonds, the so-called poly-Schiff bases[46,47], are organic polymers which contain in the main chains systems of conjugated >C=C< and >C=N– bonds as well as nitrogen atoms containing in the outer energy level electrons which are not involved in chemical binding. Poly-Schiff bases are synthesised[48,49] by the polycondensation of diamines (*p*-phenylenediamine, *m*-phenylenediamine, and benzidine) with dicarbonyl compounds (benzil) using an excess of one of the bifunctional compounds.

The influence of the molecular and supermolecular structures on the optical and photoelectric properties was studied for three types of compounds: (I) initial poly-Schiff bases; (II) hydrogenated polymers; (III) block-copolymers[50].

The initial polymers, obtained from *p*-phenylenediamine and benzil using an excess of the diamine or benzil, from *m*-phenylenediamine and benzil, and from benzidine and benzil, consist of coloured powders. The hydrogenated polymers are amorphous powders with a lighter colour than the corresponding initial polymers. The absence of degradation in the course of hydrogenation was confirmed by measurements of the molecular weights of the polymers and by infrared spectroscopy. The softening temperature of the hydrogenated polymers is reduced and their solubility is improved somewhat. The block-copolymers can be divided into two groups[48,49]. The first group includes products of the combination of dicarbonyl polyconjugated blocks with diamines. These copolymers have a lighter colour and are more soluble in dimethylformamide than the initial polymers. The comparatively low viscosities, high softening temperatures, and low solubilities of the products of the coupling of the blocks to one another are apparently due to the strong interaction between the polyconjugated blocks of different chains and the limited mobility of the blocks when they are incorporated in a polymer chain[51]. The second group of block copolymers are products of the coupling of polyconjugated blocks containing terminal amino-groups to flexible poly(ethylene glycol) blocks. With increase of the length of the flexible block, the interaction between flexible blocks and between polyconjugated blocks diminishes in this group. It is noteworthy that, by virtue of the above factors, those copolymers lose their capacity for crystallisation (they are amorphous).

In molecules with conjugated bonds containing heteroatoms, the lone electron pair of nitrogen is conjugated with the π electrons of the conjugated bond[46] and this so-called n,π conjugation, which influences the molecular geometry, obtains in addition to the π,π conjugation. The polyconjugated systems considered do not therefore constitute a single conjugation system and are made up of a collection of sections with delocalisation of electron density. The weakening of the delocalisation of electrons along the conjugation chain can occur as a result of the displacement of the system from coplanarity, the introduction of a benzidine group and *meta*-substituted benzene rings, and hydrogenation. This result is confirmed by the nature of the electronic absorption spectra. Thus the spectra (Fig. 9, curves *4–6*) clearly reveal the disappearance on hydrogenation of the long-wavelength maxima corresponding to the conjugation system (the signal characteristic of polymers with a conjugation system disappears from the EPR spectra of the hydrogenated polymers). An increase of molecular weight also weakens the

delocalisation of electrons. In the series of polymers with M = 600, 1000, and 1330 (Fig. 9) the maximum is displaced towards shorter wavelengths, from 372 to 350 nm, which indicates the occurrence of this effect.

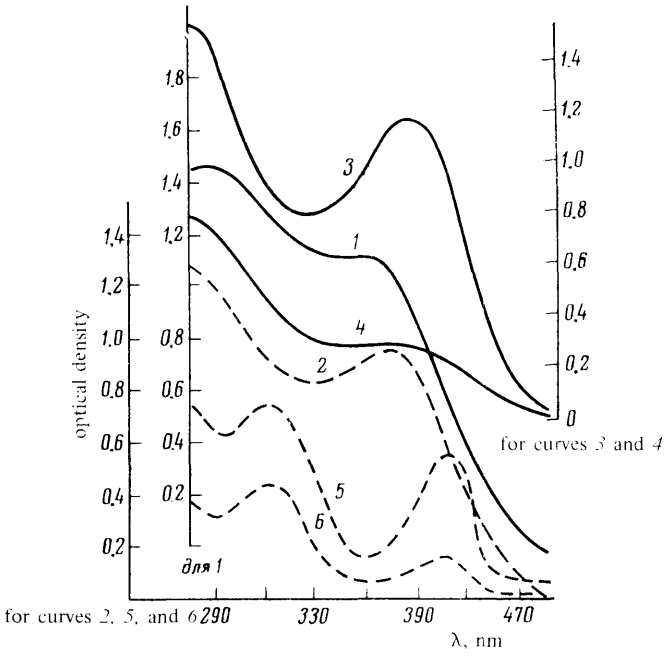


Figure 9. Absorption spectra of poly-Schiff bases with different molecular weights [1) 1330; 2) 1000; 3) 600] and hydrogenated specimens (curves 4–6).[50]

4. POLYMERIC CHARGE-TRANSFER COMPLEXES

Polymeric charge-transfer complexes (CTC) have been recently examined in a review[2]. In CTC the generation of photocarriers is associated with charge transfer from the donor to the acceptor in the molecules of the complex, accompanied by the liberation of the charge-transfer energy $E_{ct} = I - E_A - E_c$, where I is the ionisation potential of the donor, E_A the electron affinity of the acceptor, and E_c the energy of the Coulombic interaction between the ions A and D.[52] The generation of the charge carrier can be described by the following equation:

$$(D \ldots A \leftrightarrow D^+ \ldots A^-) \overset{\hbar\omega, ct}{\rightleftarrows} (D^+ \ldots A^- \leftrightarrow D \ldots A),$$

so that in the excited state the equilibrium is displaced towards the ionic form.

To a first approximation photoexcitation (or the charge-transfer energy) depends on the two quantities I and E_A and, when I = const., E_{ct} can be reduced as a result of an increase of E_A, which is equivalent to a bathochromic shift of the absorption band[53,54]. It is noteworthy that in the general case there is no correlation between the electron affinity of the acceptor in polyvinylcarbazole (PVC) complexes and the photoconductivity of the CTC for acceptors of different classes. Such correlation occurs only for acceptors with similar π-electron clouds and the relative dimensions of the donor and the acceptor can apparently play an appreciable role in this process[55–57].

(a) The Similarity of the Electronic Natures of Organic High- and Low-Molecular-Weight Photoconductors

In polymers with a conjugation system, for example in PPA, PDPA, PDPB, etc., continuous conjugation does not embrace the entire macromolecule and consists of individual conjugation sections (blocks), so that the size of the macromolecule greatly exceeds the size of the average conjugation block. The conjugation between blocks is to a large extent weakened owing to their non-coplanarity. The mechanism of the formation of conjugation blocks in the polymerisation of compounds of the acetylene series is associated with the dependence of the electronic transition energy ΔE_π on the number of π electrons.[11] Fig. 10 illustrates the dependence of ΔE_π on the number of π electrons (N_π) for α,ω-diphenylpolyenes and polyacenes.[58] Whereas in α,ω-diphenylpolyenes containing conjugated double bonds there is a tendency towards a limit and, when $n > 5$, the quantity $\Delta E \to 2.5$ eV [$\Delta E = 2.5$ for the system $R(-HC{=}CH-)_nR$, where R = CH_3 and $n = 15$ [58]], in acene systems with a slight alternation of bonds ΔE_π decreases fairly rapidly with increase of N_π and there is only a slight tendency towards a limit. The results obtained from electronic absorption spectra are confirmed by theoretical calculations by the Hückel method. For α,ω-dimethylpolyenes containing conjugated double bonds, the calculated limiting value is $\Delta E = 2.25$ eV.[59]

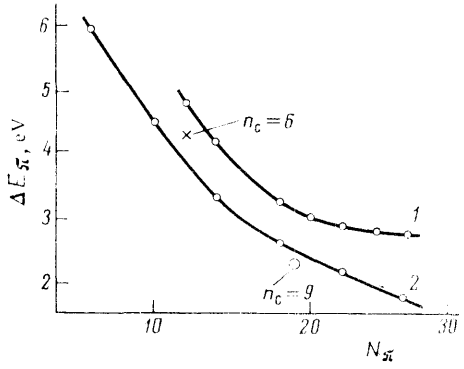


Figure 10. Dependence of the electronic transition energy ΔE_π on the number of π electrons for α,ω-diphenylpolyenes (curve 1) and acenes (curve 2). The crosses represent the activation energies for conduction in polymers with different conjugation blocks: $n_c = 6$ for PPAT, $n_c = 9$ for PPAZ and PDPB.[11]

Thus experimental data and quantum-chemical calculations show that the energy gain in diphenylpolyenes in the optical transition changes insignificantly on successive increase of the conjugation blocks and gradually tends to zero when ΔE_π approaches 2.5 eV. For definite value of

n, a non-coplanar addition of the $(n + 1)$th unit is thermodynamically favourable, which leads to the formation of a new conjugation block non-coplanar with the preceding block. Analogous conclusions are valid for acene structures.

The data examined above suggest that the extent of π conjugation necessary for specific properties of polyconjugated polymers, including photoconductivity, does not exceed the extent of conjugation in low-molecular-weight organic compounds and the electronic structures of organic high- and low-molecular-weight substances are therefore the same.

III. STRUCTURAL SENSITISATION OF THE ELECTROPHOTOGRAPHIC RESPONSE

Electrophotography (EP) is based on the possibility of the formation in the material, when the latter is charged, of an electrical double layer made up of the surface charge and the shielding charge arising in the bulk phase or the conducting base, with subsequent local modulation of its power (the product of the charge density and the thickness of the double layer) as a result of photoconductivity. The drift of the charge carriers generated by light in the electric field of the double layer leads to the neutralisation of the surface charge or to a decrease of the thickness of the double layer.

The study of the problem of the non-photoactive absorption in molecular (polymeric) photoconductors under EP conditions led to the observation of the phenomenon of the so-called structural sensitisation of the photoeffect[60]. The phenomenon consists in the dependence of the spectrum and the quantum yield of the internal photoeffect on the molecular and supermolecular structures of the photoconductor. The nature of the molecular and supermolecular structures determines the probability of the generation of free charge carriers from the first bound state on absorption of a light quantum.

We shall consider this phenomenon in greater detail for polymeric photoconductors of different classes.

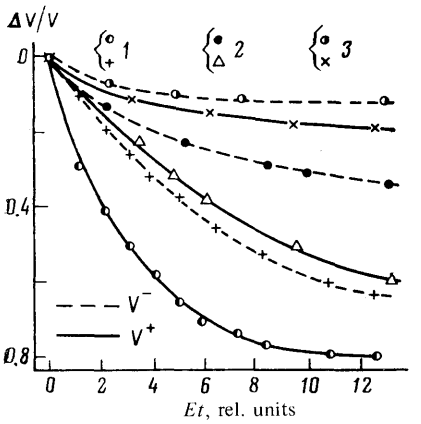


Figure 11. Monochromatic curves for the photodischarge of polystyrene EP layers (0.3 μm) [61]; λ (nm): 1) 115; 2) 147; 3) 180; Et = degree of illumination (relative units).

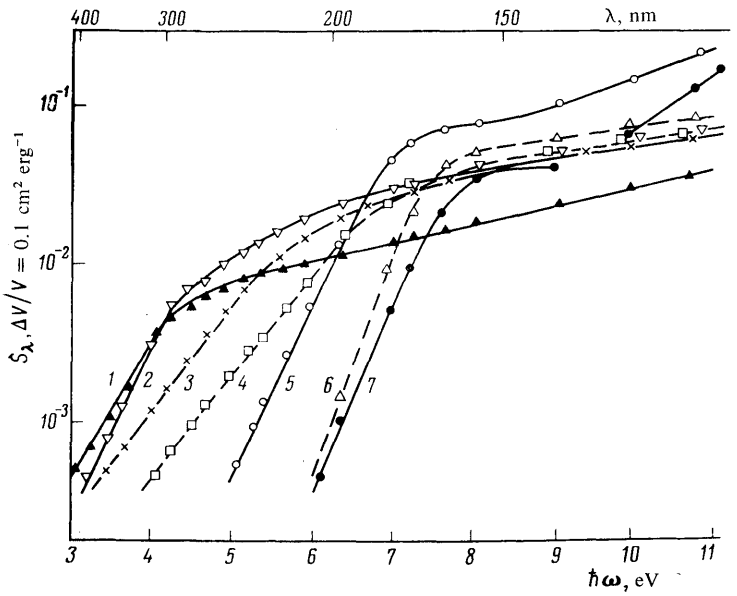


Figure 12. EP sensitivity spectra of polymer layers with saturated and conjugated bonds in the main chain constituting the basis of a catalogue of EP layers with a variable long-wavelength light sensitivity limit[61-64]: 1) polydiphenylbutadiyne; 2) polyvinylcarbazole; 3) polyphenylacetylene; 4) polyethylene; 5) polyacrylonitrile; poly(vinyl chloride); 7) polystyrene.

1. POLYMERS WITH SATURATED CARBON–CARBON BONDS

Among studies on the photoconductivity of polymers of the vinyl series with various functional groups[60-78], those devoted to the intrinsic photoconductivity occupy a special place. The phenomenon of the intrinsic photoconductivity of vinyl polymers in the vacuum ultraviolet region of the spectrum was observed in 1968 independently by two groups of investigators and was examined in two corresponding series of studies by Cherkasov and coworkers[60-65] and Ofran and coworkers[72-74].

Quantitative studies on the EP sensitivity spectra were carried out in the range 3–11 eV for polyethylene, poly(vinyl chloride), and polyacrylonitrile layers and in the range 3–21 eV for polystyrene layers[61-64]. The kinetics of the photodischarge of the EP layers based on the above polymers are characterised by curves which are asymmetric relative to the sign of the surface charge (Fig. 11). The shape of the curves depends on the wavelength: with increase of the latter, the rate of photodischarge decreases faster and the residual potential (the threshold value of the electric field for the non-photoactive absorption of light) increases. The nature of the EP sensitivity spectra of saturated polymers (as well as polymers with a polyconjugation system) in the vacuum ultraviolet region is approximately the same: the EP sensitivity depends on the sign of the surface charge and, for example, for polystyrene with a positive charge, it is greater by a factor of four than for the polymer with a negative charge. The dependence on the wavelength is more pronounced: for the same polystyrene, the EP sensitivity increases by a factor of 100–150 with decrease of wavelength by a factor of three (from 180 to 60 nm). The position of the long-wavelength limit of the EP sensitivity (Fig. 12) depends on the structure of the polymer and, for polymers of the vinyl series, is displaced towards longer wavelengths to an increasing extent in the presence of the following groups: benzene ring, chlorine, cyano-group, hydrogen, and the carbazole ring.

We may note that the above polymers (except polyethylene) are amorphous (vitreous). Polyethylene is crystalline, while polystyrene is atactic and isotactic and is capable of crystallising with a glass point at 95.5°C; poly(vinyl chloride) is atactic and has not been obtained in a crystalline form, its glass point being 80°C; polyacrylonitrile is atactic and has a flow temperature above the decomposition temperature; polyvinylcarbazole has a glass point of 117°C. In the above series the shift of the EP sensitivity limit is largely due to the shift of the absorption limit.

The study of the influence of the structure of the polymers with saturated bonds on the quantum efficiency showed (in relation to polystyrene)[61] that the latter is independent of the molecular weight in the range from 10^3 to 10^6. On the other hand, the number of double bonds in the main chain, which has been varied in a controlled manner by dehydrogenation, has a selective spectroscopic effect[61] (Fig. 13). Thus the quantum efficiency is constant in the range 120–135 nm, where valence electrons of the molecule are responsible for absorption, decreases in the range 135–180 nm with increase of the number of double bonds, and increases in the range 180–220 nm owing to the photoactive absorption by the C=C bonds of the main chain with their subsequent photodegradation accompanied by a decrease of the absorption in this part of the spectrum.

The above data on the energetic EP sensitivity of saturated polymers in the vacuum ultraviolet region made it possible for the first time to characterise quantitatively the photoconductivity phenomena and to determine in the first place the absolute quantum yield of the internal photoeffect.

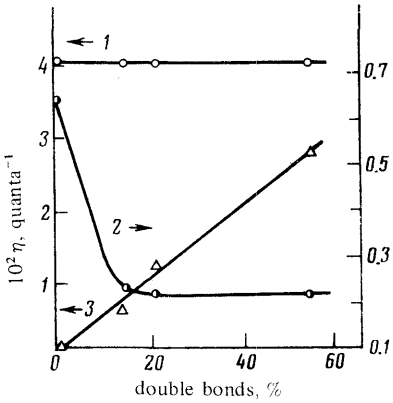


Figure 13. The selective spectroscopic effect of the change in the number of double bonds in the main chain of polystyrene on the EP sensitivity (quantum yield) of the layers[61]; $\Delta\lambda$ (nm): 1) 120–135; 2) 135–180; 3) 180–220.

Comparison of the sensitivity spectra of EP layers of polystyrene, EP layers of selenium, and photographic layers based on silver thiocyanate, developed specially for the vacuum ultraviolet region, showed[62,65] that the EP sensitivity of polystyrene layers exceeds that observed for silver thiocyanate layers and in the region of 60 nm approaches the sensitivity of selenium layers. The amount of light necessary to record the image (based on the criterion of the relative change in the potential of the EP layer $\Delta V/V = 0.1$) is 28 erg cm^{-2} at λ = 115 nm and 2.8 erg cm^{-2} at λ = 58.4 nm. The fairly high EP sensitivity of polymers of the given class in the vacuum ultraviolet region combined with a low sensitivity in the longer-wavelength part of the spectrum made it possible to reduce the background due to the scattered long-wavelength light in the recordings of images and led to the creation of a catalogue of EP layers for the vacuum ultraviolet region with a variable light sensitivity limit[66,68].

2. POLYMERS WITH CONJUGATED CARBON–CARBON BONDS

Polymers with a polyene chain (PCCP) do not exhibit EP sensitivity in the part of the spectrum under consideration, although they are charged to appreciable potentials.

For polymers with aromatic substituents (PPAT, PIPAT), the EP sensitivity and the limiting potential of the layers were found to depend on the supermolecular structure and on the presence of iodine atoms in the structure[64] (Fig. 14). Amorphous PPAT layers have a high limiting potential (both positive and negative), but their sensitivity is extremely low. The presence of iodine

atoms in PIPAT greatly reduces the limiting potential (to 5–10 V) but at the same time increases the EP sensitivity. The change of the supermolecular PPAZ structure from amorphous to crystalline (with a degree of crystallinity up to 80%) on slight decrease of the limiting potential leads to an appreciable increase of the EP sensitivity. The layers exhibit EP sensitivity in the <600 nm region of the spectrum with a maximum in the region of < 300 nm (Fig.15).

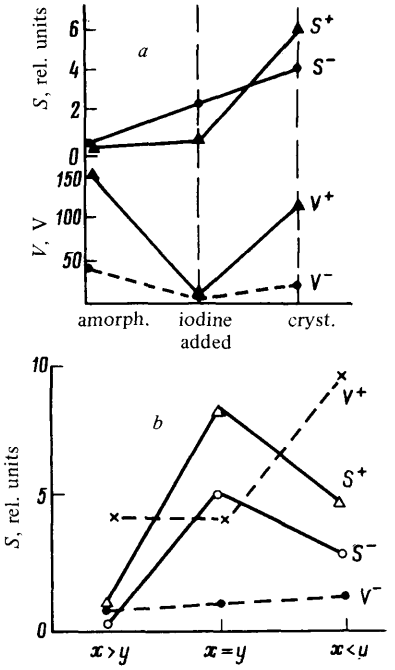
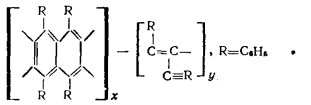


Figure 14. The influence of the structure of polymers on the EP properties of layers[64]; *S*—spectral sensitivity; *V*—limiting charging potential; *a*) polyphenylacetylene with a variable supermolecular structure and with the introduction of iodine atoms: PPAT (amorph.), PIPAT, PPAZ (cryst.); *b*) PDPB with a variable ratio of the initial components during synthesis:



The solvent has a marked influence on the EP parameters[60,64]. Aromatic solvents (toluene) are removed with much more difficulty from polymer films than solvents such as carbon tetrachloride. Thus CCl_4 is fully removed from the polymer film in the course of 4 h in a vacuum of 10^{-2} mmHg, while the complete removal of toluene requires a vacuum of 1×10^{-5} mmHg. Concentration and type of solvent do not affect the limiting potential of the EP polymer layers, but the presence of a solvent in the layer accelerates the dark relaxation of the positive potential in the polymer layers and to a greater extent at higher solvent concentrations (Fig. 16); on the other hand, the dark relaxation of the negative potential under these conditions remains almost unchanged. Rather thick (up to 10 μm) EP layers based on PPAZ, completely freed from the solvent, do not exhibit EP sensitivity in the ultraviolet and visible regions of the spectrum. The presence of a certain amount of solvent in polymer films leads to the appearance of EP sensitivity but only in positively charged PPAZ layers (Fig. 16). Thin (3 μm) PPAZ layers exhibit an appreciable EP sensitivity after the removal of the solvent (Fig. 16).

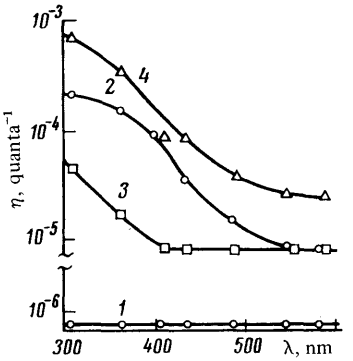


Figure 15. The spectrum of the quantum yield in layers of polyconjugated polymers[60]: 1) polychlorocyclopentene; 2) polyphenylacetylene; 3) polydiphenylacetylene; 4) polydiphenylbutadiyne.

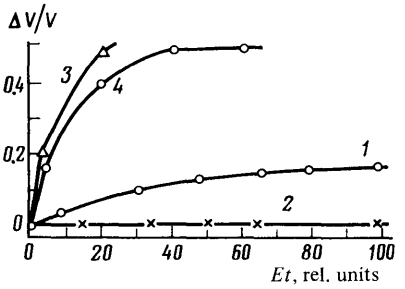


Figure 16. The retardation of the rate of photodischarge of EP layers following the removal of solvent (carbon tetrachloride) from polyphenylacetylene [64] (*Et* is the degree of illumination expressed in relative units): 1) and 3) initial layers [1) 11 μm; 3) 3 μm]; 2)–4) after the removal of the solvent.

EP layers based on polymethylethynylpyridine (PMEP) [11,64] are characterised by an asymmetry of the limiting potential and the kinetics of dark relaxation as well as the kinetics of photodischarge. The layers also exhibit a sensitivity only for a negative surface charge, which indicates the predominance of *n*-type charge carriers in the layers. The EP sensitivity is independent of the molecular weight and of the different types of treatment (polymers both soluble and insoluble in benzene have been isolated for a polymerisation temperature of 300°C).

The layers exhibit EP sensitivity in the ultraviolet part of the spectrum (< 400 nm); the sensitivity is then lower by an order of magnitude than for PPA layers (Fig. 15). The low EP sensitivity can be naturally accounted for by the high efficiency of the competing process—luminescence.

Polymers with a Double Conjugation System

The EP sensitivity of PDPB layers, obtained by casting from solution, depends on the ratio of x and y units in the structure (Fig. 14*b*). A common feature over the entire range of contents of the initial components is the asymmetry of the potential: the positive potential greatly exceeds the negative potential. The EP sensitivity varies in a complex manner: it is low for $x > y$, passes through a maximum at $x = y$, and decreases for $x < y$. The positive limiting potential then increases. The layers exhibit EP sensitivity over a wide spectral range (<600 nm) (Fig. 15) and have a broad maximum at 400–440 nm and a second maximum at shorter wavelengths.

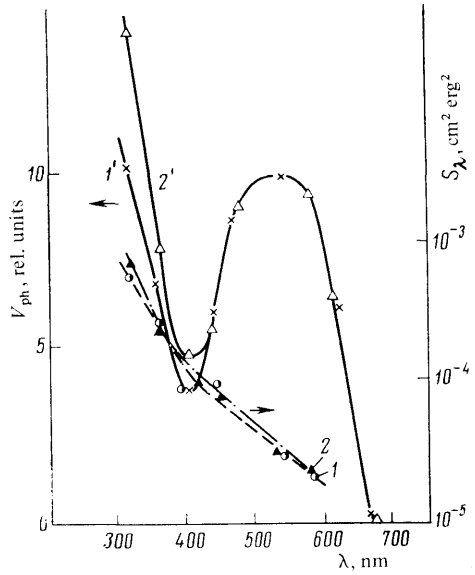


Figure 17. *EP*-sensitivity (curves *1* and *2*) and photo-e.m.f. (curves *1'* and *2'*) spectra of polydiphenylbutadiyne layers obtained from solution (curves *1* and *1'*) and by evaporation in a high vacuum (curves *2* and *2'*).[44]

A characteristic feature of polyphenylacetylene layers obtained by vacuum sputtering[44] is an increase of the mobility of charge carriers from 7×10^{-5} cm² V⁻¹ s⁻¹, a value characteristic of layers obtained by casting from solution, to 0.07–0.01 cm² V⁻¹ s⁻¹.[45,78] The energy required to generate a single electron–hole pair has been shown[45] to depend on the nature of the polymer, its structure, and the evaporation conditions; it can reach high values (300–500 eV), which indicates a complex mechanism of the generation of charge carriers.

A comparative study of the photo-e.m.f. and EP-sensitivity spectra for two types of layers (obtained from solution and by vacuum evaporation) (Fig. 17) showed that they are virtually the same and that there are therefore no differences between the quantum efficiencies of the generation in such layers. An important advantage of the layers obtained by vacuum sputtering is high optical quality, comparable to the quality of inorganic vitreous photoconductor films such as those of selenium.

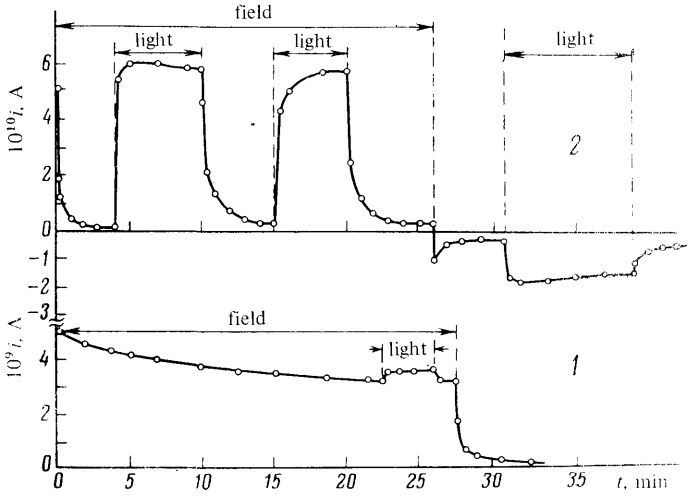


Figure 18. Kinetics of the photoconduction in PDPB layers obtained from solution (1) and by evaporation in a high vacuum (2).[44]

In conclusion we shall note yet another difference between the properties of the layers—the difference between the kinetic characteristics of the photoconductivity and polarisation phenomena (Fig. 18). The non-monotonic establishment of a stationary photocurrent (transverse photoconductivity conditions) in the course of the first illumination and the presence of depolarisation currents are characteristic of high-resistance compounds, both inorganic[79] and organic[80,81], although they have not been observed for a whole series of substances, particularly for many organic dyes[82]. In the PDPB layers of the two types under consideration these phenomena are manifested fairly clearly, which can be seen from the kinetic curves in Fig. 18.[44] When an electric field is applied, the dark polarisation-type current decreases more slowly for the layers obtained from solution. The dark current in these layers is higher by an order of magnitude than in the layers obtained by vacuum sputtering, which is correlated with the reduced "memory" under the EP conditions. Next, when the first light II-pulse is applied to a layer in an electric field, the photocurrent reaches a stationary value after passing through a maximum, although in subsequent exposures a stationary current is established monotonically (curve *2*). A monotonic form of the curve is also observed for PDPB layers of the other type (curve *1*). When the field is removed from the specimen (curve *2*), a depolarisation current is observed and in the subsequent

exposure there is a depolarisation photocurrent. For the other type of layers, depolarisation effects were not observed.

We may note that both types of layers exhibit hole conductivity, which has been established on the basis of the sign of the photo-e.m.f. and the nature of the photodischarge curves under EP conditions. The relaxation characteristics described[44] were obtained for the transverse conductivity of the layers in a field of 10^4 V cm^{-1}. Under EP conditions (longitudinal photoconductivity) in fields of 2×10^5 V cm^{-1}, such slow kinetic effects are not manifested, although a tendency towards polarisation effects can be responsible for the decrease of the EP sensitivity with decrease of field strength.

3. POLYMERS WITH CONJUGATED CARBON–NITROGEN BONDS

Polymers of this class exhibit an electrical conductivity of $10^{-10} - 10^{-13}\ \Omega^{-1}$ cm^{-1}. Their EP properties vary within wide limits depending on the molecular and supermolecular structures[50]. Under these conditions, the light relaxation curves for layers based both on the monomers and on the polymers have two sections—with rapid and slow rates of relaxation and a fairly high residual potential.

Layers based on monomers (benzylideneaniline, 2,3-diphenylquinoxaline, and dibenzylidene-*p*-phenylenediamine) have low limiting electric field strengths and do not exhibit an appreciable photoeffect. The introduction of the benzidine group into benzylideneaniline or *meta*-substituted benzene rings leads to an appreciable increase of the limiting field strength (up to 20 V m^{-1}). At the same time EP sensitivity appears in the ultraviolet. The maximum quantum efficiency is 1.5×10^{-5} quantum^{-1}.

Layers based on poly-Schiff bases have a limiting field strength which varies within wide limits (10–200 V μm^{-1}). Almost all the polymers sensitised exhibit EP sensitivity in the ultraviolet. Its magnitude increases, as for the monomers, when a benzidine group or *meta*-substituted benzene rings are introduced into benzylideneaniline. Polymers obtained from *p*-phenylenediamine and benzil with an excess of the diamine exhibits the highest limit sensitivity (quantum efficiency 1×10^{-4} quantum^{-1}), whereas the quantum efficiency of polymers obtained with an excess of benzil is lower (4×10^{-5} quantum^{-1}). The EP sensitivity is almost independent of the length of the molecular chain but depends strongly on the regularity of the supermolecular structure: for many polymers in the crystalline state, it is higher by an order of magnitude than in the amorphous state. It is noteworthy that hydrogenation also leads to the appearance of light sensitivity in amorphous polymers and block copolymerisation both increases and decreases the light sensitivity of the initial polymers.

We may note a characteristic feature of the above monomeric and polymeric layers, which consists of the "memory" of the previous history of the layer. In contrast to the familiar instances of "memory" in organic photoconductors, characterised by a monotonic variation of the light sensitivity, for polymeric photoconductors of the above class the memory involves relations with an extremum, for example, in the limiting potential and in the EP sensitivity of the "memory" layers and in the number of charging-exposure cycles. The light sensitivity of such layers passes through a maximum[50].

The observed characteristics of the influence of the molecular and supermolecular structures on the photoconductivity can be interpretated within the framework of the following general ideas. The photocurrent depends on the conditions governing the generation, transport, and recombination of charge carriers and all three stages can depend on the molecular and supermolecular structures. In particular, an enhancement of the delocalisation of electrons along the conjugation chain of the molecule and an increase of the regularity of the supermolecular structure should, by improving the transport conditions, lead to an increase of light sensitivity. As shown above, light sensitivity does indeed increase with increasing regularity of the structure (on transition from the amorphous to the crystalline state).

The nature of the possible influence of the molecular structure is more complex. The experimentally observed increase of the quantum efficiency of polymers when the delocalisation of electrons along the conjugation chain is weakened (primarily by the introduction of the benzidine group and *meta*-substituted benzene rings) is apparently associated with the increase of the efficiency of the generation of electron–hole pairs, which proceeds via an exciton stage. The impairment of the conditions for the transport of free carriers in this instance is probably not of decisive importance for the EP sensitivity in consequence of the presence of a strong electric field, which is responsible for the appreciable migration of the carriers even when their mobility is low. However, the regularity of the structure in the case of exciton generation can alter significantly the diffusion distance of the excitons, reducing the probability of their decomposition (accompanied by the generation of free carriers) and thereby influencing actively not only the transport stage but also the stage in which charge carriers are photogenerated.

IV. SPECTRAL SENSITISATION OF THE ELECTROPHOTOGRAPHIC RESPONSE

The spectral sensitisation of polymers is of considerable interest not only from practical but also from theoretical points of view[55,83-87]. The current hypotheses concerning the mechanism of spectral sensitisation are based on two alternative process mechanisms[88-90]: involving the transfer of excitation energy from the dye molecule to the photoconductor, under the influence of which a free charge carrier subsequently appears, or the transfer of a photoelectron to the excited dye molecule. There is at present no unambiguous experimental evidence in support of one or other mechanism, but, presumably, if the excitation energy transfer mechanism operates in a substance with exciton generation of photocarriers, then the spectral sensitisation can be regarded as the "pumping" of the energy absorbed by the dye into the sensitised photoconductor; the quantum yield η in the sensitisation region is then determined by the value of η of the sensitised photoconductor. Organic polymeric photoconductors with exciton generation of photocarriers then exist under very unfavourable conditions, since their quantum yield of the internal photoeffect in the visible region is low, which is due to fundamental causes arising from the exciton generation mechanism[60]. The conditions governing the dissociation of excitons can be made easier and the quantum yield increased by the formation of charge-transfer complexes from the initial polymers.

In the study of sensitisation, two extreme cases, differing in the concentration of dye molecules in relation to the sensitised polymer or the CTC based on it, are of interest. The first case involves high concentrations of carriers. The greatest number of studies have been devoted to it and extensive data have now been obtained for the quantum yields in the generation of photoholes from complexes based on polyvinylcarbazole (PVCA) on sensitisation with triarylmethane and pyrylium dyes, monomethinecyanines, and trimethinecyanines.[1,91] The quantum yield in the region of sensitisation reaches 50%. However, the use of high concentrations of dyes and CTC makes the system heterophase; an opalescence usually appears and the resolution diminishes. Such a system does not exhibit thermomechanical properties important for applications in a photothermoplastic EP process.

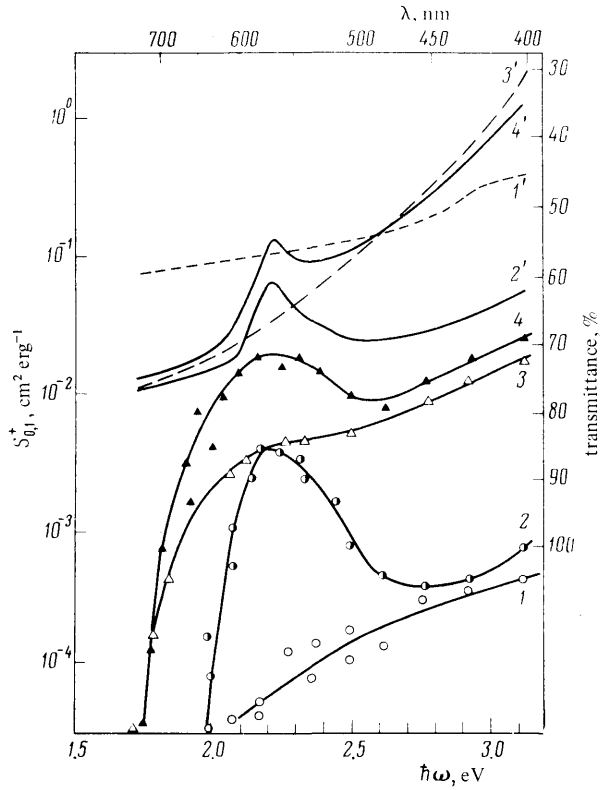


Figure 19. EP-sensitivity spectra of PVCA (curve *1*) and PVCA–TNF charge-transfer complex (curve *3*) layers; 2) and 4) corresponding layers sensitised by rhodamine B; 1′)–4′) transmission spectra of layers *1*–*4* respectively[92] ($S_{0,1}$—spectral sensitivity in absolute energy units).

The above disadvantages can be eliminated by reducing the concentrations of CTC and dyes (second case), but the nature of the phenomenon can then be significantly altered. As in the first case the formation of complexes and the sensitisation of PVCA by dyes causes a significant increase of the EP sensitivity of PVCA [92] (Fig.19). In order to examine the nature of the effect, we turn to Fig.20, which illustrates the absorption spectra and the spectral sensitivity of optically homogeneous layers of PVCA and its complexes as well as layers sensitised by rhodamine B.[93] Fig. 20 shows that the charge-transfer complex exhibits a broader absorption region than the initial polymer and a much higher light sensitivity (curve *3*). One need only note that the efficiency in relation to the absorbed energy at the maximum does not exceed 20% (taking into account the reflection). The sensitisation by rhodamine B increases by a factor of ~15 the light sensitivity of the polymer and by a factor of 5 that of its charge-transfer complex. The absolute quantum yields of the internal photoeffect at the 567 nm absorption maximum (in the presence of a superimposed electric field of 7×10^{-5} V cm^{-1}) are as follows:

Layer	PVCA	CTC	PVCA sensitisation by rhodamine B	CTC sensitisation by rhodamine B
η, %	~1	3.3	1.1	3.6

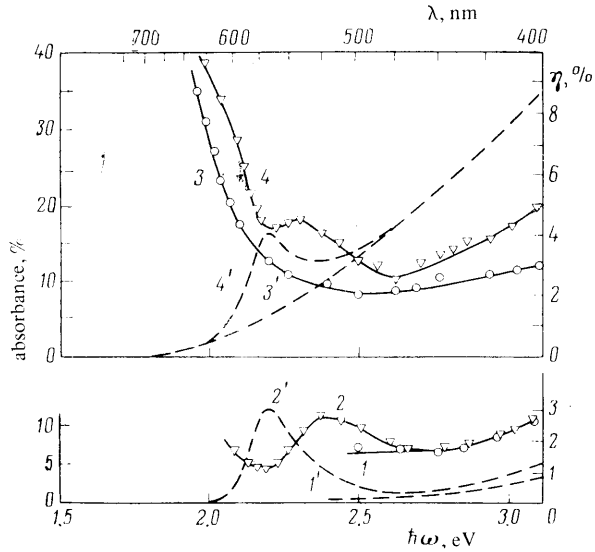


Figure 20. Quantum yield spectra (η is the absolute quantum yield of charge carriers per quantum, %) of the internal photoeffect (curves *1*–*4*) and the absorption spectra (curves *1′*–*4′*) of PVCA (curves *1* and *1′*), PVCA sensitised by rhodamine (curves *2* and *2′*), PVCA–TNF charge-transfer complex (curves *3* and *3′*), and PVCA–TNF charge-transfer complex sensitised by rhodamine B (curves *4* and *4′*) [93]; dye concentration 0.28 mole %; trinitrofluorenone concentration 3.2 mole %.

Thus the efficiency of the sensitisation, defined as the ratio of η at the sensitisation maximum to η for the initial polymer, remains constant and close to 100% despite the different initial values of η. The relation obtained shows that the mechanism of the spectral sensitisation in the case of exciton generation under consideration is due to the "pumping" of energy into the polymer by the dye. In both instances of sensitisation examined, its efficiency must therefore be regarded as a maximum and the light sensitivity is limited solely by the fraction of energy absorbed in the layer.

We may note that, as can be clearly seen from the experimental data (Fig. 20, curves *3* and *4*), the introduction of a dye leads to an increase of the quantum yield not only in the region of the sensitisation of the CTC but also in the region of shorter wavelengths, which may be evidence for the formation of complexes in the PVCA–dye systems. In this sense, the sensitisation of PVCA by dyes leads to the possibility of increasing the quantum yield over a much wider region of the spectrum in the short-wavelength range compared with the absorption spectrum of the sensitiser dye.

V. INJECTION SENSITISATION OF THE ELECTROPHOTOGRAPHIC RESPONSE

The increase of light sensitivity and the extension of the region in which it occurs for polymeric photoconductors can be achieved by injection sensitisation based on the phenomenon of photoinjection in film heterostructures. The principle of the construction of heterostructures with EP sensitivity makes it possible to control the properties of the layers, in the sense of extending the width of the region of spectral sensitivity and improving the memory, and ensures the thermoplastic visualisation of the latent image in the presence of the appropriate thermomechanical properties of the component which does not carry the photogeneration function[94]. Among all the possibilities enumerated above, the case of high light sensitivity achieved by the photoinjection of carriers, which ensures their transfer through the heterostructure, is of greatest interest.

A heterostructure with EP sensitivity is nowadays achieved on the basis of inorganic systems, because an organic component as a rule gives rise to a potential carrier, which prevents injection[95]. A system containing selenium and PVCA is exceptional in this respect[96,97], but here injection has been observed only from heterophase *p*-selenium, which did not ensure a high resolution.

High-resolution heterostructures based on amorphous forms of selenium and thermoplastic compositions based on PVCA have been investigated recently[94]. The heterostructures were made in glass frames with a conducting layer of lead dioxide on which layers of *n*- and *p*-type selenium and PVCA 0.1–0.3 μm thick were deposited in succession. The study of dark EP properties of the above heterostructures showed that, for the negative surface charge corresponding to the injection of holes into PVCA, the associated limiting field strength (3×10^5 V cm^{-1}) corresponds to that observed for selenium layers and the dark relaxation time corresponds to that for PVCA layers. The retention of properties indicated above (in contrast to, for example, selenium–polystyrene heterostructures[95]) indicates the absence of an energy barrier at the inner boundary of the heterostructures when a field (of definite polarity) is imposed. The absence of a barrier is important for ensuring the possibility of the transfer of carriers, generated in selenium, through the heterostructure and, according to preliminary EPR data, can be associated with the formation of a charge-transfer complex at the selenium–PVCA boundary. In fact, on the one hand, the ability of polycyclic aromatic systems, including PVCA, to form charge-transfer complexes with electron acceptors is known and, on the other hand, the ability to add an additional electron to the electron shell is characteristic of atoms with an unfilled outer electron shell (the *p*-shell in selenium is unfilled).

The shape of the photodischarge curves confirms the photoinjection of holes and the absence of the injection of electrons. Injection is observed from both *p*- and *n*-type selenium, which is due to the mixed nature of the photoconductivity of the two forms of selenium. At any rate, an electron-hole pair is initially photogenerated in selenium after which carriers predominating in PVCA (holes) are injected through the boundary and transported through PVCA.

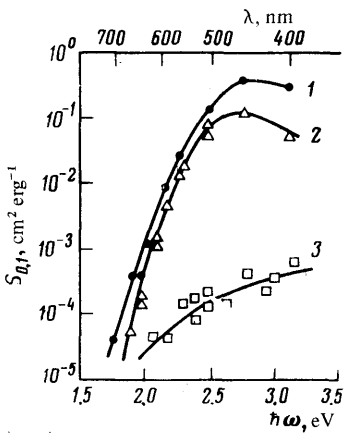


Figure 21. EP-sensitivity spectra of PVCA layers (2 μm thick) in injection sensitisation by selenium [94]: 1) *p*-Se (0.2 μm); 2) *n*-Se (0.3 μm); 3) no selenium.

The light sensitivity of the heterostructure significantly exceeds that of PVCA and in the region of strong absorption virtually corresponds to the light sensitivity of selenium layers, decreasing with increase of the wavelength owing to the decrease of the absorption of energy (Fig. 21), while the quantum yield η corresponds to η for amorphous forms of selenium over the entire spectral range investigated. The data in Fig. 21 were obtained for a field strength of 3×10^5 V cm^{-1}. The light sensitivity depends markedly on the field over the entire range of the spectrum and, in contrast to PVCA, there is a critical field of $\sim 6 \times 10^4$ V cm^{-1} for the heterostructure, below which there is no light sensitivity. If it is assumed that the traps in PVCA are small and that a space charge does not therefore arise on photodischarge, the threshold field can be interpreted as the field necessary to ensure the photoinjection of charge carriers from selenium into PVCA. The dependence of the light sensitivity of *n*-type selenium on the field can be naturally accounted for by the dependence of η on the field[60], or, in the case of *p*-type selenium, it is probably associated with the dependence of the conditions for the transport of carriers on the field.

Thus photoinjection in the heterostructures examined makes it possible to combine the high light sensitivity of selenium with the effective thermomechanical properties of compositions based on PVCA, which ensures the resolution of an element whose size does not exceed the wavelength of visible light when the light sensitivity is high.

VI. THE QUANTUM YIELD AND THE STRUCTURE OF POLYMERS

Systematic studies have demonstrated a fundamental difference between the spectra of the quantum yield of the internal photoeffect in polymeric photoconductors and classical semiconductor crystals such as those of germanium and silicon. Whereas the quantum yield in the above semiconductor crystals (which represents the number of free charge carriers generated by a single absorbed quantum) is constant over a considerable range of energies of the quantum and close to 100% up to the absorption limit, in polymeric photoconductors it is close to zero in the region of the absorption limit, increasing in the interior of the absorption band[60]. The photogeneration of charge carriers over a wide range of energies of the quanta via the state involving a Coulombically bound electron–hole pair (exciton) plays a decisive role in the establishment of the structure of the quantum yield spectrum. The probability of the separation of the pair depends on the kinetic energy of the electron which has absorbed the quantum and on the rate of loss of this energy. The reverse recombination of the electron with its "own" hole or its "own" ion, which leads to a non-photoactive absorption, takes place as a result of the decrease of the kinetic energy of the electron to the thermal energy level before the electron moves outside the limits of the sphere of the Coulombic field of its partner in which the electron attraction energy exceeds the $\frac{3}{2}kT$ level. The external electric field facilitates the photogeneration process by reducing the Coulombic barrier and increasing thereby the probability of the escape of the carrier (the Frenkel–Poole effect).

We shall now consider the spectra of the quantum yield of the internal photoeffect in anthracene single crystals, polyconjugated polymers of the same electronic type as anthracene (polymers of the acetylene series), and saturated polymers having the same composition as anthracene (polystyrene and other polymers of the vinyl series).

Unique possibilities for the investigation of the absolute quantum yield of the internal photoeffect arise under EP conditions. To achieve such conditions, an ionic contact is made with the surface of the layer located on a conducting support. The density of the ionic charge, generated by the ionisation of air molecules, reaches 10^{12} cm^{-2} for an average interionic distance of 100 Å. Such contact ensures optical transparency over the entire experimental part of the spectrum and the maximum possible electric field strength which is not limited by the "weak sites" in the layer in view of the absence of longitudinal conductivity and which makes it possible to obtain saturation currents for substances with a low mobility of charge carriers such as the photoconductors investigated. Furthermore, the ionic contact ensures a virtually complete exclusion of an external photoeffect in the ultraviolet, which is limited to the strong fields of the electrical double layer formed, reaching 10^6 V cm^{-1}.

The number of charge carriers n generated by light is related to the change in the potential of the layer ΔV when the carriers have been completely collected, by the expression

$$n = \varepsilon \cdot \Delta V/4\pi de|_{\Delta V \to 0},$$

where ϵ is the dielectric constant and D the effective thickness of the layer. The condition $\Delta V \to 0$ ensures a quasi-stationary potential. One of the fundamental difficulties when the EP method is used involves demonstrating the complete collection of carriers; several pieces of evidence in support of this claim can be adduced:

(1) the presence of a linear section on the photodischarge curve.

(2) Direct calculation of the shift of charge carriers. Thus a 100% collection coefficient for electrons and holes was ensured in single-crystal anthracene layers 15 to 20 μm thick[51]. The mobility of holes $\mu_g = 5 \times 10^{-1}$ cm^2 m^{-1} s^{-1}, $E = (2-20) \times 10^4$ V cm^{-1}, and $d = 20$ μm; the time of flight of holes $t_{fl} = d/\mu E = (2-20) \times 10^{-8}$ s is much shorter than $\tau_g = 3 \times 10^{-5}$ s (τ_g is the lifetime of holes); the electron mobility $\mu_e = 3 \times 10^{-1}$ cm^2 V^{-1} s^{-1} and the time of flight of electrons $t_{fl} = (3-30) \times 10^{-8}$ s^{-1} $\tau_e = 2 \times 10^{-6}$ s.

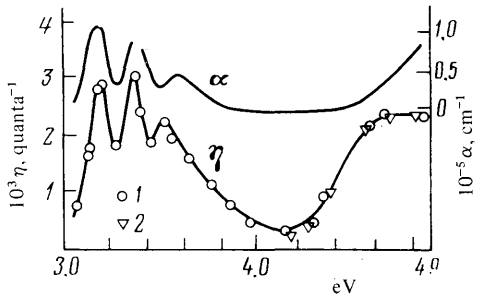


Figure 22. Absorption (α) and quantum yield (η) spectra of a single-crystal layer of anthracene[51,61]: 1) holes; 2) electrons; $E = 2 \times 10^5$ V cm^{-1}.

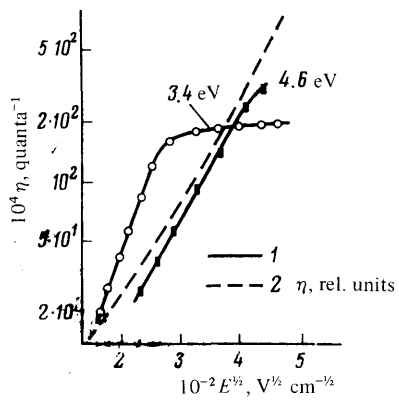


Figure 23. Dependence of the quantum yield for anthracene layers on the electric field[60]: 1) experimental data; 2) calculated data.

For polystyrene (PS) layers, we have $\mu_g = 10^{-4}$ cm^2 V^{-1} s^{-1}, $E = (4-15) \times 10^5$ V cm^{-1}, $d = 0.3$ μm, and $t_{fl} = (2-8) \times 10^{-7}$ s $< \tau_g = 1 \times 10^{-6}$ s (estimate under EP conditions from $\mu\tau$ for $\eta = 100\%$). For polyacetylene layers, particularly for polydiphenylacetylene, $\mu = 5 \times 10^{-4}$–6.5×10^{-5} cm^2 V^{-1} s^{-1}, which also ensures a complete collection of carriers.

(3) Whereas it is known that in the region of strong absorption 100% collection of carriers is ensured, in the region of weak absorption, which softens the collection conditions, the collection can also be complete. A decrease of light sensitivity with decrease of absorption coefficient is in this case caused solely by a change in generation conditions.

An exceptional value of η close to 100% can also serve as evidence for complete collection.

In order to eliminate the influence of space charge in the measurement of $\eta(E)$, a family of photodischarge curves at different initial potentials was obtained. It is noteworthy that, when η depends on E, a linear photodischarge plot is not observed even in the region of complete collection ($\mu\tau E = d$) (the current is not saturated).

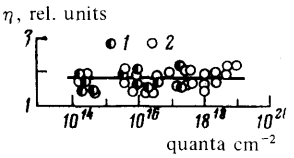


Figure 24. Dependence of the quantum yield for an anthracene layer on the ionisation density[95] ($E = 2 \times 10^5$ V cm^{-1}): 1) 3.4 eV; 2) 4.1 eV.

For anthracene, the spectrum of η values in the region of energies of the quanta $\hbar\omega$ less than the width of the forbidden gap $E_g = 3.9$ eV is associated with the diffusion of molecular excitons (with a small radius) to the surface and corresponds to the optical absorption spectrum (Fig.22). In the region where $\hbar\omega > E_g$, η increases with increase in $\hbar\omega$. In both regions the photogeneration is controlled by the electric field (Fig. 23). The influence of the field cannot be associated with the change in the conditions for the recombination of free carriers, since there is no dependence of the quantum yield on the ionisation density within the limits of five orders of magnitude (Fig. 24) and the change in the saturation of generation centres as the field strength is varied in the region of $\hbar\omega < E_d$ would lead to a decrease of η with increase of the field.

The effect of the field in the region of molecular excitons indicates the existence of an intermediate state in the formation of free carriers as a result of the interaction of the exciton with a centre (in anthracene this can be oxygen) having a high electron affinity and weakening the electron–hole interaction of the Coulombically bound electron-hole pair. The probability of the escape of one of the carriers of the pair from the stationary (in the interaction with the centre) or mobile partner is determined by the electric field (Fig. 23). There is a threshold quantum energy $\hbar\omega \simeq E_g$, above which there is a finite probability that the primary pair gives rise to free carriers as a result of an excess energy equal to $\hbar\omega - E_g$. In this region η is therefore independent of the absorption coefficient α and increases with increase of $\hbar\omega$. In the region where $\hbar\omega < E_g$ it is necessary to supply an additional energy to the pair in order to cover the energy deficiency; in the given instance this energy is drawn from the crystal lattice (the generation centres). For the operation of this mechanism, the bound pair (exciton) must be mobile if the generation centres are mainly in the surface region. The difference between the dependences of η on the field in the two regions, namely the occurrence of saturation and a different slope of the $\eta(E)$ relation when the Frenkel–Poole law $\lg\eta \propto E^{1/2}$ holds over a wide range of E values in the given model, can be explained by the limited number of generation centres, so that all the excitons interacting with the centres in fields of 2×10^5 V cm^{-1} give rise to free carriers. The change in the slope of the $\eta(E)$ line is due to the change of the constant in the Frenkel–Poole equation: in the region where $\hbar\omega < E_g$ charge carriers escape from the stationary centre (in this region only holes are mobile), while in the region where $\hbar\omega > E_g$ the carriers move away from one another ($\eta_e \simeq \eta_h$).

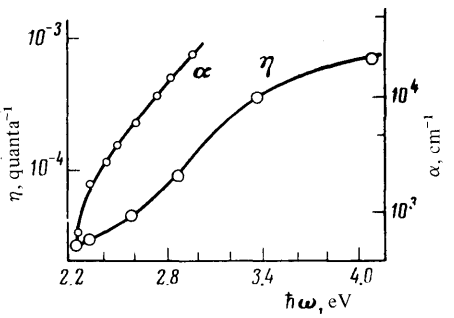


Figure 25. Absorption (α) and quantum yield (η) spectra for PDPB layers[95].

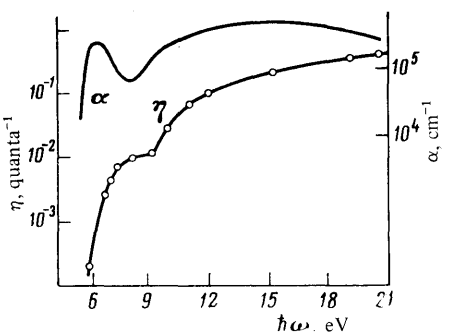


Figure 26. Absorption (α) and quantum yield (η) spectra for a polystyrene layer[15].

Polyacetylenes (Fig. 25—polydiphenylbutadiyne) and polymers of the vinyl series (Fig. 26—polystyrene) in the amorphous state are also characterised by a value of η which increases with increase of $\hbar\omega$ and E. The maximum value of η for PDPB is of the same order of magnitude as the value for molecular crystals (this question is discussed in greater detail elsewhere by one of the authors of the review[60]).

The relations obtained indicate the occurrence of exciton effects in molecular, crystalline, and amorphous photoconductors, which lead to a broad region of non-photoactive absorption at the edge of the spectrum. The probability of the decomposition of the primary bound states arising following the absorption of a light quantum depends on the structure of the photoconductor, which leads to the possibility of the structural sensitisation of the photoeffect.

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