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The synthesis and properties of *N*-(2,3-epoxypropyl)carbazoles and the oligomers based on them

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ABSTRACT. **The principal methods of synthesis of *N*-(2,3-epoxypropyl)carbazoles and the oligomers based on them, their physicochemical optical, photophysical, and electrical properties, as well as the practical applications of carbazole-containing polymers are examined.**

The bibliography includes 177 references.

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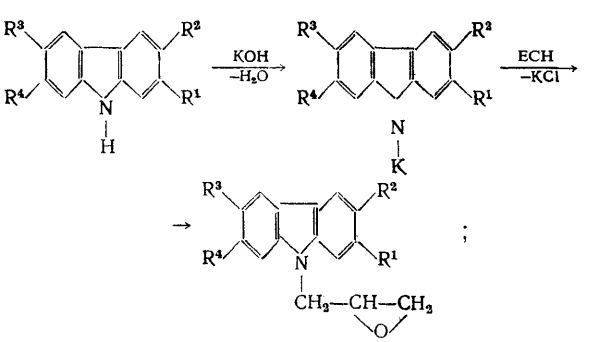
I. Introduction

In connection with the development of technical means for the recording, storage, and reproduction of information, there has been recently an appreciable growth of demand for new non-silver photographic processes, among which electrophotographic processes occupy a notable place. One of the thermoplastic materials with fairly high chemical, radiation, and thermal stabilities as well as effective electrically insulating properties and most widely used in electrophotography is poly-*N*-vinylcarbazole (PVCA).[1] The electrophotographic materials based on PVCA are light, can be readily charged (positively and negatively), are fairly transparent, and have an effective resolving power. On the other hand, the high softening temperature, low adhesion to different substrates, and poor film-forming properties characteristic of PVCA hinder its wide-scale employment in electrophotography. Since the photoelectric properties of PVCA are determined primarily by the presence and relative disposition of carbazole groups, presumably, on passing from carbochain polymers to polyethers containing analogous substituents with extensive systems of conjugated bonds, the photoelectric properties of the system will not change significantly. As a result of the appearance of ether linkages in the main chain of carbazole-containing polymers, one should then expect a decrease in the softening temperature and an improvement in the adhesion and film-forming properties. One of the cheapest and most promising types of photosemiconducting polyethers used as thermoplastic materials in electrophotography are poly-*N*-epoxypropyl carbazoles (PEPC), obtained by the polymerisation and copolymerisation of *N*-(2,3-epoxypropyl)carbazole (EPC) and its derivatives.

Although little more than 10 years have elapsed since the appearance of the first communications on the synthesis of EPC derivatives and oligomers based on them, fairly extensive information has accumulated in the literature on the synthesis, structures, and the physicochemical and photophysical properties of such materials. These results have been reflected in one way or another in a series of reviews devoted to questions of the synthesis and properties of carbazole-containing polymers.[1–4] In writing the present review, the authors endeavoured as far as possible to arrange systematically and analyse the available information (including patent data) on the synthesis and properties of monomeric and oligomeric EPC published after 1973.

II. Methods of synthesis and properties of *N*-(2,3-epoxypropyl)carbazoles

Epoxypropylcarbazoles are obtained by treating the corresponding *N*-metallated carbazole with epichlorohydrin (ECH) in accordance with the following scheme:



R^1—R^4 = H, Br; R^1 R^4 = H; R^2, R^3=Cl; R^1, R^2, R^4=H, R^3=NO_2.

The reaction is carried out in benzene,[5] ethyl methyl ketone,[6] a mixture of xylene isomers,[8] or dimethylformamide.[9–11] According to Sazonenko et al.[9] and Inaki et al.,[10] the potassiocarbazole formed initially reacts subsequently with epichlorohydrin to form EPC. Since potassiocarbazole is readily hydrolysed in the presence of water, the water evolved in the interaction of carbazole with potassium hydroxide retards the formation of potassiocarbazole and hence EPC.

EPC is also obtained by fusing carbazole together with KOH at 200–250 °C with subsequent treatment of *N*-potassiocarbazole with epichlorohydrin in benzene.[5] The interaction of carbazole and its derivatives with epichlorohydrin in the presence of alkalis has been studied by Rovkina.[7] It has been shown that the interaction of carbazoles with epichlorohydrin can be achieved under mild conditions and in one stage in dipolar aprotic solvents in the presence of solid alkalis. The formation of two types of substances was observed under the conditions investigated—*N*-(2,3-epoxypropyl)carbazoles and dicarbazolylpropanols, the process comprising consecutive stages with respect to epichlorohydrin and parallel stages with respect to carbazole. The selectivity of the conversion of carbazole into the products indicated is mainly influenced by the carbazole: epichlorohydrin ratio.

The low yield of the target product (up to 24%), the long reaction time,[8] the formation of 1,3-di(*N*-carbazolyl)-2-propanol as a side product, and the consumption of large amounts of solvents in the purification of EPC[6] are significant disadvantages of the above methods of synthesis of EPC.

Much better results have been obtained in the reaction of carbazole with sodium ethoxide and epichlorohydrin in purified dimethylformamide (DMF)[11] and also in the presence of substances forming hydrates such as alkali metal carbonates and sulphates.[12] Under these conditions (30–40 °C, 20–30 min), the target product is obtained in 99% yield.

Table 1. Characteristics of epoxypropylcarbazoles.

Monomer	M.p., °C	Method of preparation
EPC*	111–112	[8]
	108–109	[5, 9]
	108	[6]
	110–111	[10, 11]
	112–113	[12]
BEPC**	54–56	[14]
DBEPC*	149–150	[13]
	145–147	[14]
TBEPC**	154–156	[14]
CEPC*	72–73	[11]
DCEPC*	143–144	[11]
NEPC**	146–148	[13]
GBC**	107	[15]

* White crystals. ** Yellow crystals.

Epoxy-derivatives of carbazole have been obtained by the reaction of substituted carbazoles with epichlorohydrin in the presence of KOH: 3-chloro- and 3,6-dichloro-EPC (CEPC and DCEPC), 3-nitro-, 3-bromo-, and 3,6-dibromo-EPC (NEPC, BEPC, and DBEPC), 3,6,8-tribromo-EPC (TBEPC), and 1,3,6,8-tetrabromo-EPC derivatives (data in Table 1). *N*-Glycidyl-7*H*-benzo[*c*]carbazole (GBC), capable of giving rise to polymers and copolymers with a higher diffraction efficiency, was obtained by treating the lithio-derivatives of 7*H*-benzo[*c*]carbazole with epichlorohydrin.[15]

Epoxypropylcarbazole and its derivatives are crystalline substances soluble in tetrahydrofuran, DMF, acetone, dimethyl sulphoxide, aromatic hydrocarbons, and chloroform. All the monomers are insoluble in alkanes and are sparingly soluble in ether and alcohols.

After the isolation of the epoxy-derivatives of carbazole from the reaction mass, they were purified by both recrystallisation[5–15] and by sublimation. The optimum conditions for the sublimation of EPC have been published.[13] Under the selected optimum conditions, an EPC with a high degree of purification and m.p. 113 °C was obtained.

Qualitative[6,11,16] and quantitative[17,18] methods for monitoring the reactions of carbazole and its derivatives with epichlorohydrin by thin-layer chromatography (TLC) have been developed.

The IR absorption bands of EPC derivatives have been assigned.[19] The UV absorption maxima of substituted EPC undergo a bathochromic shift relative to EPC and to a greater extent the more polar the substituent in the carbazole nucleus.[14,20]

Measurements have been made of the photocurrents and dark currents in EPC.[20] The dark currents I_d for EPC, DBEPC, and NEPC are respectively 1.5×10^{-12} A (at 3 V), 1.2×10^{-13} A (at 14 V), and 5.5×10^{-11} A (at 7 V). The ratios of the photocurrent to the dark current (I_{ph}/I_d) at 4 V and for a light energy $W = 6.8 \times 10^{-3}$ W cm^{-2} are respectively ~5, 10, and 20 for EPC, DBEPC, and NEPC.

III. Certain characteristic features of the synthesis of *N*-(2,3-epoxypropyl)carbazole oligomers

The most important properties of epoxypropylcarbazoles are their ability to polymerise on treatment with catalysts with opening of the epoxide ring and the formation of linear oligoethers. Methods are known for the synthesis of oligomers and cooligomers of epoxypropylcarbazoles by their polymerisation in the presence of anionic, cationic, and coordination catalysts and also by the chemical modification of oligomers and by polymer-analogue transformations.

1. Anionic polymerisation

EPC are known to polymerise on treatment with anionic catalysts such as potassium hydroxide,[10,21–23] sodium phenoxide,[24,25] dimethylbenzylamine,[26] triethylamine and water,[7,27] sodium *p*-nitrophenoxide,[28] and the radical-ion salt of sodium and naphthalene (SN),[29,30] zinc acetate and aluminium isopropoxide,[31] and potassium t-butoxide.[32]

The study of the polymerisation of EPC in both homogeneous and heterogeneous media has shown that the polymerisation takes place most effectively in a heterogeneous medium,[21,23,26] especially in bulk on treatment with KOH. The polymerisation of EPC in bulk on treatment with KOH depends to a large extent on the state of the catalyst surface.[21–23] The rate of polymerisation and hence the yield of the polymers are higher when the polymerisation is carried out using finely dispersed KOH.[33]

The kinetic curves for the heterogeneous polymerisation of EPC in bulk on treatment with KOH[21,23,33] indicate the absence of an induction period in contrast to polymerisation on treatment with SN[30] and sodium *p*-nitrophenoxide.[28] The rate of polymerisation which increases with increase in temperature and catalyst concentration is independent of the initial stage and monomer concentration, subsequently diminishes for high degrees of conversion.

The rate of polymerisation of EPC at 120 and 140 °C and for catalyst concentrations ranging from 1 to 8 mol% are 1.38×10^{-4} and 4.84×10^{-3} s^{-1} [21] and 1.0×10^{-3} and 2.0×10^{-3} s^{-1}.[33]

As on initiation by treatment with SN,[30] the introduction of a fresh portion of the monomer after its quantitative conversion in the first stage leads to a non-linear increase in the degree of polymerisation as a function of the degree of conversion of the monomer and to a slight broadening of the molecular weight distribution. Thus, after the formation of the EPC polymer (140 °C, yield 92%) with a number-average molecular weight $\overline{M}_n$ = 1100,[33] the repeated introduction of the monomer results in the formation of a product with $\overline{M}_n$ = 1560 in 90% yield. A similar picture has been observed in studies[21] where $\overline{M}_n$ for the polymer formed in the first and second stages was 1560 and 2300 respectively.

The study of the polymerisation of EPC in a homogeneous medium[24,28–32] and in particular in DMSO in the presence of potassium t-butoxide[32] indicates a high initial rate of the process and its subsequent diminution. According to the authors, the main cause of this is the large difference between the rates of initiation and chain propagation as a consequence of the appreciable nucleophilicity of the t-butoxide ion compared with the nucleophilicity of the active centre. The PEPC obtained on treatment with the above catalysts contains in its structure hydroxy- and propenyl end groups as well as a small number of allyl end groups, formed as a result of the partial isomerisation of the propenyl end groups.[34] It has been shown that hydrolysis of the unsaturated propenyl ether end groups by concentrated hydrochloric acid results in the formation of hydroxy-groups.

On the other hand, the low molecular weights of the EPC polymerisation products obtained in the presence of KOH and other anionic catalysts, the absence of a linear increase in $\overline{M}_n$ with the degree of the conversion of the monomer, the non-proportional increase in the molecular weight after the addition of a fresh portion of the monomer, the presence of unsaturated end groups in PEPC, and also the difference between the calculated and experimental molecular weights indicate chain transfer in the polymerisation process. It has been suggested that chain propagation is stopped by chain transfer to the monomer[21–23,30–33] and, in the case of polymerisation of EPC in dimethyl sulphoxide (DMSO) on treatment with alkali metal alkoxides, also as a result of chain transfer to the solvent.

However, in the polymerisation of EPC on treatment with alkali metal phenoxide in an aprotic solvent (dioxane) in the presence of dibenzo-18-crown-6, it has been possible to reduce the factor associated with chain transfer to the monomer and to obtain PEPC with $\overline{M}_n$ = 4300.[24]

Among the EPC derivatives, poly-3,6-dibromo- and poly-3-nitro-EPC (PDBEPC and PNEPC)[33] and poly-3-chloro-, poly-3-methyl-, and poly-3-acetyl-EPC[34] have been obtained by the anionic mechanism. In the polymerisation of DBEPC in the presence of KOH, the reaction order with respect to the catalyst is 2/3 with a polymerisation process activation energy of 79 kJ mol^{-1}.[33]

2. Cationic polymerisation

N-(2,3-Epoxypropyl)carbazole and its derivatives polymerise[9,35,41] and copolymerise[37,42,43] fairly vigorously in the presence of cationic catalysts. The increased reactivity of EPC derivatives in polymerisation reactions on treatment with boron trifluoride etherate[35,37–40] and tin tetrachloride[36,38] can be accounted for by the electro-donating contribution of the substituent, which promotes an enhancement of the electron density on the epoxy-group.

A characteristic feature of the cationic polymerisation of EPC is the high rate of reaction in the initial stage and the rapid attainment of the limiting degree of conversion of the monomer, which increases with increase in the catalyst concentration. It has been established that, in the polymerisation of EPC in the presence of $BF_3.OEt_2$, the reaction orders with respect to the monomer and the initiator are 1.0 and 0.9 respectively, while the polymerisation rate constant is described by the equation:

$$K = 6.7 \cdot 10^2 \exp\left(-\frac{3.73 \cdot 10^3}{RT}\right). \quad (1)$$

The molecular weight of the oligomers in the cationic polymerisation does not exceed 2000 and depends little on the catalyst concentration. The limitation of the molecular weight in the polymerisation process is caused by the high contribution of the chain transfer reaction and by the deactivation of the active centres.[37] In the polymerisation of EPC in the presence of $SnCl_4$ in dichloroethane, the initial rate of reaction is directly proportional to the monomer and initiator concentrations and the molecular weight of PEPC increases on reducing the temperature and with increase in the initial monomer concentration.[38]

The higher glass point of the EPC oligomers obtained in the presence of $BF_3.OEt_2$ compared with the oligomers synthesised in the presence of KOH can be explained by the presence of macrorings in the PEPC structure.[39]

3. Other methods of synthesis of the oligomers

EPC oligomers and cooligomers have been obtained on treatment with $ZnEt_2$ and $AlBu^n_3$ [35] and also by means of polymer-analogue transformations[44–46] and by the chemical modification of the PEPC structure.[27,47–49] A high-molecular-weight PEPC has been synthesised[44] with a high degree of conversion by the reaction of the potassium or sodium salt of carbazole with polyepichlorohydrin.

The interaction of the terminal OH groups of PEPC with bi-functional reagents such as dichloromethylphenylsilane and 2,4-tolylene diisocyanate[45] leads to carbazole-containing block copolymers exhibiting a high photosensitivity and diffraction efficiency.[45] Block copolymers of EPC with epichlorohydrin and glycidyl dihydroabietate have been obtained by the reaction involving chain transfer to the polymer with dissociation. In each case, the polymerisation of one of the monomers was carried out in the presence of the other oligomer.[46] However, the analogous statistical cooligomer of glycidylcarbazole (GC) with epichlorohydrin exhibits a higher photosensitivity as a result of the formation of a more effective charge transfer complex (CTC) in this case. The statistical block copolymers of EPC with NEPC (in the presence of KOH as the catalyst) have been described.[13] The chemical modification of PEPC[43,47–49] and of its brominated derivatives[48] constitutes a route to materials with electrophotographic sensitivity over a wide spectral range, which are promising for use in electrophotography. The formyl derivative of PEPC has been condensed[47] with 2,4,5,7-tetranitrofluorene and 6-methyl-2,4-diphenylpyrylium at 30 – 100 °C.

The oligomers obtained were compatible with PVCA and PEPC in any proportions, affording uniform films with a photosensitivity up to 650 nm.

The molecular weights of the cooligomers based on EPC and its di- and tri-bromo-derivatives with butyl glycidyl ether (BGE) are close to those of the EPC homopolymers, while the molecular

weights of the cooligomers of EPC with allyl glycidyl ether are significantly higher. The cooligomer films exhibit two physico-mechanical and optical properties and more effective adhesion to various substrates.[43,48] The integral photosensitivity of the EPC cooligomers increases linearly with increasing fraction of the comonomer.[48] Thus the cooligomer of DBEPC with BGE, sensitised by 9-dicyanomethylene-2,4,7-trinitrofluorene (DCMTNF) has a sensitivity higher by a factor of 4–5 in the range 600–700 nm than that of the unmodified PDBEPC.[43,48] Bromo-substituted PEPC, which have been tested under holographic recording conditions (λ = 633 nm) on layers 1.0–1.5 μm thick with sensitisation by trinitrofluorene, have a diffraction efficiency up to 20%.[48]

4. Some characteristics of the polymerisation of epoxypropylcarbazoles

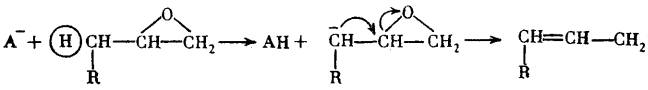
The study of the anionic polymerisation of EPC and its derivatives has shown that SN is a less effective initiator[30] than other catalysts of polymerisation in a homogeneous medium.[24,28,29,31,32]

The nitro-derivatives of EPC do not polymerise on treatment with SN, which is associated with the ease of electron transfer from SN to the nitro-group of the monomer; this has been confirmed by the results of a polarographic study: the half-wave potentials $E_{1/2}$ for NEPC and naphthalene are respectively −1.28 and −2.53 V. DBEPC partially polymerises in the presence of SN with elimination of sodium bromide. The elimination of bromine is also promoted by electron transfer from the SN molecule to DBEPC with the apparent subsequent formation of the DBEPC carbon ion.[50] The partial elimination of bromine with formation of KBr has also been observed in the polymerisation of DBEPC on treatment with solid potassium hydroxide at high temperatures.[33]

The induction period in the polymerisation of EPC in the presence of SN is apparently associated with the formation of low-molecular-weight polymeric alkoxides and with their insolubility in THF and also with the possibility of electron transfer from SN to the carbazole nucleus. The induction period depends on the initiator concentration and the polymerisation temperature, diminishing as the latter increase.[30]

Since gel-permeation chromatographic data rule out the degradation of the polymer chain, the low molecular weights and the absence of a linear relation between $\overline{M}_n$ and the degree of conversion are evidence for chain transfer to the monomer, which is so significant for substituted epoxides.[51]

According to Akhmedov et al.,[30] unsaturated terminal groups are formed as a result of chain transfer to the monomer via the proton β-elimination mechanism:[52]



R = N-carbazolyl.

The study of the polymerisation of EPC in the presence of SN in solution in THF at catalytic complex concentrations in the range 6.1×10^{-3}–1.2×10^{-1} M suggests that the polymerisation proceeds via a stepwise anionic mechanism. Initiation at high initial initiator concentrations is effected by dianions, while at lower concentrations it is initiated by comparable amounts of the mono- and di-anions. The polymerisation is of the living centres type,[53] i.e. in the presence of material chain termination reactions but with propagation of kinetic chains.

The rate of polymerisation of EPC on treatment with KOH should be described by the following equations in the initial polymerisation stage:[13]

$$W = \frac{d[M]}{dt} = k_1 \cdot [M]_0^0, \quad (2)$$

$$W = k_2 [KOH]^n, \quad (3)$$

where W is the rate of polymerisation in the initial stage, [M] the monomer concentration at time t, $[M]_0$ the initial monomer concentration, t the polymerisation time, k_1 and k_2 are polymerisation rate constants, [KOH] is the catalyst concentration, and n the reaction order.

The experimental data indicate a satisfactory fulfillment of the law $W \propto [KOH]^{2/3}$ in the initial stage, which agrees with the occurrence of the reaction on the interface.[13]

The zero reaction order in the initial stage of the polymerisation with respect to the monomer is evidently associated with the fact that the fraction of the catalyst surface covered by the monomer is close to unity and the rate therefore ceases to depend on the monomer concentration.

The decrease in the rate of polymerisation after the attainment of a definite degree of conversion of the monomer, which is particularly abrupt at low initial catalyst concentrations, is associated with the accumulation in the system of an inactive oligomer, which prevents the access of the monomer to the catalyst surface. This is confirmed by the fact, when the EPC polymerisation is carried out in the presence of an EPC oligomer obtained in an independent experiment, the degree of conversion of the monomer in the initial stage diminishes sharply. When the catalyst is kept beforehand in contact with oligomers obtained in an independent experiment, the polymerisation of the monomer introduced subsequently is inhibited, which indicates the "coating" of the catalyst by the polymerisation products.[33] The above features are somewhat different from those in the polymerisation of EPC in the presence of KOH with vigorous stirring.[21]

The occurrence of the preferential chain transfer to the monomer and not to another reactant with a mobile hydrogen atom (for example, water when aqueous alkali is used as the catalyst, or the polymer) is confirmed by the fact that, in the polymerisation of EPC on treatment with anhydrous EPC, products with a low molecular weight, containing large amounts of propenyl end groups, are also formed. Treatment of the alkaline polymer with an equal amount of polymer obtained in an independent experiment does not increase the degree of unsaturation of the system. However, treatment of the alkaline polymerisation mixture at a ~100% degree of conversion with a fresh portion of the monomer leads to an increase in the degree of unsaturation.[33]

IV. The properties of *N*-(2,3-epoxypropyl)carbazole oligomers

1. Physicochemical properties

The products of the polymerisation of EPC are oligomers with a molecular weight up to 2000, which consist of colourless powders readily soluble in aromatic and chlorinated hydrocarbons, DMF, THF, and acetone and insoluble in alcohols and alkanes.

Depending on the molecular weight, the glass points T_g of the EPC oligomers are in the range 70–105 °C [54,55] and for equal molecular weights are appreciably lower than the T_g for PVCA obtained both by the polymerisation of *N*-vinylcarbazole[56] and by the transvinylation reaction.[57] This can be explained by the increase in the flexibility of the PEPC chain owing to the presence in the macromolecule of ether linkages and the removal of bulky carbazole substituents from the main chain of the oligomer as a result of the introduction of the methylene group.

The dependence of T_g on the weight-average molecular weight M_w for PEPC obtained in the presence of $SnCl_4$ and the $Al(OPr^i)_3-ZnCl_2$ mixture is very pronounced for low values of M_w, becoming less marked for M_w above 2500, and not being manifested at all for still higher values of M_w.[55] When $M_w \simeq 10^4$, one may expect the formation of a thermomechanical segment which depends on the method of synthesis of PEPC.

The products of the cationic polymerisation of EPC (in the presence of $SnCl_4$ or $BF_3.OC_2H_5$) have higher glass points T_g than the polymers with similar M_w obtained in the presence of other catalysts, which has been attributed to intramolecular and intermolecular donor–acceptor interactions between the residues of the catalyst bound covalently to PEPC and the carbazole groups. Another explanation of this finding may be the formation in the first case of cyclic structures, as has been observed for PVCA.[58] Indeed, it has been shown that, in the cationic polymerisation of EPC using $BF_3.OEt_2$, between 31 and 48% of oligomeric cyclic structures are formed.[42] The glass points of the EPC oligomers with molecular weights in the range from 800 to 1800, obtained in the presence of the SN complex, increase from 90 to 100 °C and are almost identical with the T_g of oligomers having the same molecular weights but obtained on treatment with KOH.[54] For similar molecular weights, the T_g of PDBEPC and PNEPC are higher by 10–15 °C than in the case of the unsubstituted PEPC, which is apparently associated with the increase in the polarity of the substituted carbazole groups.

Oligomeric PEPC has been analysed by X-ray diffraction[59] and a study has been made of the relation between its photosemiconducting properties and its phase state. The diffractometer traces of all the oligomers show, regardless of the methods of their synthesis, only an amorphous halo with a maximum at scattering angles $2\theta = 20-21°$ and signs of crystallinity are completely absent. The phase state of the oligomeric PEPC is not affected by the character of the end group (hydroxy-groups, unsaturated groups, and cyclic groups) and also by the heat treatment of the PEPC specimens for 1 h at temperatures up to 150 °C. It has been suggested that PEPC has an atactic molecular structure. It has been shown that the absence of crystallinity of PEPC in anionic polymerisation can be associated with the occurrence, together with the β-dissociation, also of the α-dissociation of the epoxide ring, while in cationic polymerisation it is associated with the formation of cyclic structures, which lead to the breakdown of the structural crystallisation condition.

The physicochemical properties of PEPC have been investigated in order to create thermodynamic foundations for the technology of electrophotographic materials based on it.[60] A study was made of the heat capacity of PEPC ($\overline{M}_n = 1200$) in the temperature range 0–350 K. In the temperature range 320–340 K, the heat capacity increases abruptly under constant pressure by an amount 0.413 J $g^{-1}K^{-1}$, which is associated with the devitrification of the oligomer. The T_g of PEPC determined in this way was 335 K. The heat capacity at room temperature was 1.121 J $g^{-1}K^{-1}$.

The thermal stability of EPC, its oligomer, and PEPC, stabilised by the Santonox-P and Bisalkophen-MCP antioxidants, has been studied by the derivatographic method.[61] It was shown that the ease of the thermo-oxidative degradation in PEPC compared with the monomer indicates the presence in the oligomer of impurities which accelerate this process.

Thin-layer chromatography of the EPC polymerisation products[62] made it possible to discover whether or not the unreacted monomer is present and also to determine the molecular weight distribution in the PEPC. The mechanism of the formation, the molecular weight distribution, and the separation of the oligomeric EPC with $\overline{M}_n$ up to 15000 by gel permeation chromatography have been investigated.[63]

2. Optical and photophysical properties

The study of the electronic spectra of free and sensitised PEPC layers and of the influence of UV radiation on the latter in air, the analysis of the photochemical oxidation products, and also the study of the photochemical reactions in polymers help to elucidate the mechanism of the photophysical phenomena occurring in processes involving the optical recording of information. The electronic absorption and luminescence spectra of PEPC and of its brominated derivatives have been studied[13,20,64–69] both in solution and in thin films. The absorption in PEPC is associated with the presence of carbazole nuclei and is determined by the allowed transitions between the singlet levels of the π electrons. The long-wavelength absorption band in the spectra of EPC oligomers is at 345 nm, while the remaining bands correspond to wavelengths of 295, 262, and 237 nm, the maxima in the absorption spectra of the thin layers undergoing a bathochromic shift by 2–4 nm compared with the maxima in the absorption spectra of the solutions. For the bromo-substituted PEPC oligomers,[69] the long-wavelength absorption band maximum has undergone a bathochromic shift compared with the unsubstituted PEPC, which is associated with the change in the electronic structure of the carbazole chromophore after the introduction of bromine atoms into its nucleus. The influence of structural factors on the formation of CTC in solution by the carbazole fragments of PEPC and its derivatives containing electron-accepting substituents with 2,4,7-trinitro-fluoroenone (TNF), 9-dicyanomethylene-2,4,7-trinitrofluorene (DCMTNF),[70] and triarylpyrylium tetrafluoroborate (TAPS) has been observed.[71,72] It has been found that the broad charge transfer band in the spectra of CTC of PEPC with TNF has $\lambda_{max} = 500$ nm and does not shift after the introduction of substituents into the carbazole nucleus, while the band for the CTC of PEPC with DCMTNF lies in the range 550–625 nm depending on the nature of the substituent. Furthermore, the introduction of electron-accepting substituents into the carbazole nucleus diminishes the equilibrium formation constant of the CTC. Comparison of the stability constants and the enthalpies ΔH of the complexes of PEPC with TAPS, TNF, and 2,4,5,7-tetranitro-fluoroenone (TENF) shows that the TAPS molecules in the CTC exhibit weaker electron-accepting properties.[71]

The luminescence of layers and solutions on irradiation with UV light is characteristic of EPC oligomers. The luminescence spectrum of PEPC depends greatly on the solution concentration. The spectra show maxima at 358 and 386 nm associated with the phosphorescence of the monomeric units and maxima at 408 and 427 nm associated with the emission by excimers,[66,67] the intensity of the glow of which increases with decrease in temperature. The luminescence quantum yield in PEPC at room temperature is $\varphi = 0.25$ and increases with decrease in temperature, which is

apparently associated with the decrease in the probability of non-radiative transitions. As the number of substituents in the carbazole nucleus increases, the emission band maxima in the luminescence spectra undergo a bathochromic shift and for di- and tri-bromo-PEPC consist of a broad band with λ_{max} = 391 and 396 nm respectively, while for tetrabromo-PEPC they are actually located at λ_{max} = 399 nm. The fluorescence spectra of layers of bromo-substituted PEPC with TNF, TENF, and DCMTNF show broad emission bands in the range 500–800 nm associated with the formation of CTC.[67] It is known[73] that in organic semiconductors the carrier generation processes are influenced significantly by the products of photochemical reactions. It has been found that, after exposure to the joint action of oxygen and UV radiation, films of bromo-substituted PEPC undergo photochemical oxidation, which diminishes the fluorescence intensity. Films of poly-tetrabromo-EPC are most sensitive to the action of UV light in air. The decrease in the intensity of the fluorescence emission band in the range 500–800 nm after prolonged UV irradiation (for more than 3 h) has been explained by the decomposition of the CTC and the partial degradation and cross-linking of the oligomer.[67]

On the basis of the study of the products of the photochemical oxidation of various PEPC specimens, attempts have been made to establish the mechanism of this process and its relation with the photosensitivity and the spectroscopic and electrophotographic parameters of layers of EPC oligomers.[74–78] When specimens of PEPC and of its brominated derivatives are UV-irradiated in air, the absorption in the wavelength range 360–600 nm increases, a long-wavelength band appears, and the optical densities of all the absorption bands in the region of the electronic transitions in the carbazole rings diminish, which has been attributed to the formation of carbazole *N*-oxides.[75,76] It has been shown that the intensity of the 1735 cm^{-1} absorption band in the IR spectra of the oligomers obtained in the presence of KOH increases with time and eventually becomes constant when the unsaturated end groups disappear, while the intensity of the 1715 cm^{-1} band increases monotonically.[75,76] Since the absorption bands at 1715 and 1735 cm^{-1} correspond solely to the carbonyl groups, it has been suggested that the photochemical oxidation products may be, together with structures of the ketone type, also quinone imide structures (band at 1715 cm^{-1}), from which units containing several carbonyl groups in the carbonyl nucleus may be formed subsequently. The molecular weight and the degree of polydispersity of the oligomers increase somewhat in highly photochemically oxidised PEPC specimens, which has been explained by the possibility of their cross-linking either via double bonds in the presence of unsaturated end groups or via carbonyl groups in the absence of unsaturation.[76]

Data obtained in studies of the electronic structures and photochemical reactions under the influence of UV irradiation in air of thin PEPC films sensitised by small amounts of added TNF, TENF, DCMTNF, and chloranil (CA) have been published.[77,78] In pure and sensitised PEPC specimens, an increase in absorption (darkening) is observed in the range 350–600 nm, becoming more pronounced as irradiation becomes more prolonged. It has been shown that the highest sensitivity to UV irradiation and hence relatively rapid ageing is exhibited by specimens of pure PEPC whose resistance to irradiation increases by a factor of almost 1.5 after the introduction of 1 mol% of sensitiser. It has also been shown[77,78] that the photochemical oxidation products, formed in the surface layer of the film, have electron-accepting properties and influence significantly the fluorescence intensity of PEPC films. The photochemical oxidation products in the PEPC layers are regarded as effective electron-accepting impurities which play a definite role in the mechanism of the photogeneration of current carriers.[79] The degree of electronic interaction between carbazole groups in photoconductors has been studied by proton and magnetic resonance (^{1}H NMR).[80] An upfield shift of the signal due to the aromatic protons of the carbazole chromophores, characteristic of PVCA, was not observed in the ^{1}H NMR spectra of PEPC solutions. The ^{1}H NMR spectra of PEPC do not differ from those of *N*-ethylcarbazole used as a model compound. A strong electronic interaction between the π-electron systems of the chromophoric nuclei in the ground state has not been observed in solutions of PEPC and of poly(*N*-carbazolylethyl glycidyl ether) by ^{1}H NMR, which has been explained by the greater difference between the carbazole chromophores and by the flexible character of the main chain. It has been suggested that, in solutions of this polyether and of PEPC, the carbazole nuclei can rotate freely about the methylene linkage in contrast to the rigid-chain PVCA.[80]

The manifestation of photosensitivity and the occurrence of a series of photophysical processes in the UV region in PEPC and its derivatives are determined primarily by the presence of the carbazole side group. In the visible region of the spectrum, PEPC does not exhibit photosensitivity.[65] In the early studies, it was already noted[81] that the photosensitivity in carbazole-containing polymers, in particular in PVCA, in the visible region is associated with the formation of donor–acceptor complexes in which the carbazole group functions as the electron donor and the impurity functions as the electron acceptor. It has been found that the photoconductivity of PVCA and of its derivatives is influenced by various electron-donating and electron-accepting additives as well as dyes. It has been shown that a correlation between the photosensitivity and the electron affinity of the sensitiser occurs only in series of electron-accepting compounds with similar π-electron systems. The most effective sensitisers for PVCA and its derivatives are TNF [82] and pyrylium, benzopyrylium, and thiapyrylium salts.[83]

Similar results were obtained in the study of the electrophotographic, optical, and photophysical properties of layers based on PEPC and some of its modified derivatives. In organic PVCA and PEPC semiconductors, there are no bands and hence the ideas of the classical band semiconductors are not applicable to them. In these semiconductors, the carriers apparently move via a jump mechanism, within the framework of which attempts have been made to account for the mechanism of the transport and photogeneration of charge carriers.[84] The photogeneration mechanism is closely related to the mechanism of the sensitisation of these semiconductors, i.e. to the energy transfer from the excited sensitiser molecule in the organic semiconductor and with the generation of a charge transfer state. The mechanism of the charge generation in layers of PEPC photochemically oxidised to different extents under electrophotographic conditions and of the influence on the photosensitivity of such layers by impurities of different kinds (initial carbazole, the monomer, the catalyst residue, and the solvent) has been described.[76] It has been established that the layers obtained from the more oxidised PEPC also have higher photosensitivities. The primary photophysical processes,[85–92] the photogeneration quantum yields,[93–98] and the drift mobilities of the charge carriers[99–104] in pure PEPC layers and PEPC layers sensitised by various additives have been investigated.

The study of the stationary photoconductivity and fluorescence, taking into account the influence on them by an external magnetic field, in PEPC layers with added dyes[87,88,91] has shown that excited charge transfer complexes participate in the current carrier generation

process both in the intrinsing absorption region and in the sensitisation region. The dissociation of the charge transfer complexes is facilitated by the external electric field and by the exciplexes formed by the interaction of the excited state of the dye with the chromophoric group of the oligomer. The dissociation of the complex with formation of current carriers takes place in its vibrationally relaxed state. The study of the characteristic features of the volume photoconductivity in thin PEPC layers sensitised by TNF[88] permitted a conclusion concerning the nature of the appearance of photogenerated current carriers in the region of the CTC absorption. Very interesting results have been obtained by studying and comparing the photophysical properties of PEPC and its brominated derivatives sensitised by different electron acceptors.[90–92] Pure layers of brominated PEPC are less photosensitive than the non-brominated PEPC in the UV region of the spectrum for positive charges and for an electric field strength of 5×10^7 V cm^{-1}. It was found previously[75–78] that, under real operating conditions, the photosensitivity of layers of PEPC and its derivatives is influenced significantly by UV radiation and oxygen (photochemical oxidation process) and that a decrease in the degree of oxidation of oligomers reduces the photosensitivity and the quantum yields of the generation of charge carriers in the UV region of the spectrum.[76]

The oxidation and photochemical oxidation of the carbazole group with formation of electron accepting quinone imide structures, which are ultimately responsible for the decrease in photosensitivity, are hindered in brominated PEPC. Predominately singlet excitons are responsible for the generation of charge carriers in brominated PEPC. The study of the quantum yield β[93–96,98] and of the characteristic features of the photogeneration and recombination of current carriers[97] in pure PEPC and PEPC sensitised by different additives has shown that, when pyrylium salts are used as sensitisers, the yield β in PEPC layers for an electric field strength $E \simeq 10^6$ V cm^{-1} increases to 0.36, whereas for the unsensitised specimen $\beta = 2.7 \times 10^{-2}$. The power dependence of β on E with an exponent of 1.2×3.3, depending on the wavelength and the nature of the sensitiser, has been demonstrated.[95,98] For PEPC layers with a 20% content of a binder and sensitised with 3 mol% of TNF, the power exponent increases from 2.3 to 3.3 when the temperature is reduced from +50 to −60 °C for $E = 10^6$ V cm^{-1} at an exciting light wavelength $\lambda = 295$ nm. In sensitised PEPC layers, the activation energy for the photogeneration of carriers (ΔE) depends only slightly on the exciting light wavelength and increases from 0.039 to 0.13 eV with decrease in the electric field strength from 1.6×10^6 to 4.0×10^5 V cm^{-1}. The increase in β with increase in the TNF concentration is caused by the improvement of electron transfer conditions.[96]

The characteristic features of the drift mobility of charge carriers have been investigated in PEPC[65,99–103] and also in a mixture of PEPC with PVCA.[104] It has been established[100,101] that in PEPC layers electrons remain stationary and the drift mobility of the majority current carriers (holes) depends to a large extent on the temperature and the electric field strength, reaching 7.5×10^{-6} cm^{2}V^{-1}s^{-1} for layers 1.5–4.5 μm thick and $E = 5 \times 10^5$ V cm^{-1}. The distances between the carbazole rings in pure PEPC are 6.8 Å, which is greater by 0.4 Å than in PVCA.[105] Evidently the increase in the drift mobility in PEPC relative to that in PVCA can be explained by the decrease in the distance between the carbazole nuclei in PEPC as a consequence of their displacement from the equilibrium position by 2–3 Å in the direction in which the electric field strength acts with increase in the probability of the transfer of the carrier between them.[100] The drift mobility of holes in PEPC layers diminishes with increase in the acceptor (TNF) concentration. After the introduction of 10 mol% and more of the acceptor, the drift mobility of the electrons can be measured. It becomes approximately equal to the mobility of holes in the presence of 50 mol% of the acceptor. The activation energies for the drift mobility in PEPC layers for electric field strengths of 4.5×10^5 and 1.5×10^5 V cm^{-1} are respectively 0.24 and 0.32 Ev.

The photoconductivity of EPC oligomers increases significantly and is manifested over a wider spectral range in the presence of optical and chemical sensitisers. Optical sensitisation is observed after the introduction of dyes into the oligomer at low concentrations as a result of the absorption of light by the dye molecules in the visible region, while chemical sensitisation is effected after the introduction of electron acceptors, which usually absorb in the UV region of the spectrum. The sensitisation of the photosensitivity of EPC oligomers by added organic dyes,[106–121] electron acceptors,[122–126] and compounds specially synthesised for the sensitisation of PEPC[127–132] has been investigated.

The study of the characteristic features and mechanism of the sensitisation of EPC oligomers by dyes,[109,111,113,114,116] nitrofluorenones,[122,124] and pyrylium salts[113,118,120] has shown that the effectiveness of the sensitisation of PEPC by TNF acyloximes[124] and arylpyrylium salts with perchlorate and tetrafluoroborate anions[114,119] greatly exceeds that of the sensitisation by TNF and TENF both in the intrinsic absorption region and in the long-wavelength region. The strong sensitising effect of pyrylium salts has been explained by the ability of pyrylium cations to bind in PEPC electron-donating impurities which generate centres for the adhesion of holes.[114] The low effectiveness of the sensitisation of PEPC by certain dyes (rhodamine 6G) compared with pyrylium salts has been attributed to the fact that aromatic amino-groups in the dye molecules create deep carrier capture centres in the PEPC layers. However, when up to 1 wt.% of boron trifluoride etherate is introduced into the system, the photosensitivity increases fivefold and reaches the level for pyrylium salts. The increase in the sensitising capacity of the above dyes after the introduction of Lewis acids has been explained by the binding of the amino-groups in the dye molecules and hence by the decrease in the concentration of deep carrier capture centres.

3. Electrical properties

The study of the electrical properties of PEPC and its complexes with various additives helps to obtain additional information for a deeper understanding of photoelectric processes, for the estimation of molecular parameters, and for the elucidation of the mechanism of the polarisation in the dark discharge of electrophotographic layers.

Fairly numerous studies have been devoted to the electrophysical properties of polymers based on *N*-vinylcarbazole and its derivatives.[1,2] However, the available literature data on the electrical properties of oligomers based on EPC are extremely scanty.

The electrical properties of free PEPC films and PEPC films sensitised by low-molecular-weight additives have been investigated.[133–135] The dielectric properties, polarisation effects, and their temperature dependence have been described.[136–138] In the study of the temperature dependence of the parameters of a galvanic cell in the Au–PEPC–Al system, ionic conduction was observed in PEPC. It was shown that the Au–PEPC–Al system forms a galvanic cell, whose e.m.f. is $E_0 = 150$ mV in the initial instant, the Au electrode being charged positively. It has been assumed that the e.m.f. in the

above system is due to oxidation-reduction reactions on the metallic electrodes and indicates the presence of an ionic component of the electrical conductivity, whose nature is associated with low-molecular-weight impurities or with the dissociation of polymer macromolecules in the solvent.[133]

The dependence of the dark current on the potential for PEPC films with added TNF obeys Ohm's law up to an electrical field strength of 10^3 V cm^{-1}. For higher field strengths, there is a break in the voltage–current characteristic and a power dependence of the current I on the applied potential U is observed with an exponent of 2.2. The non-linearity of the voltage–current characteristic is attributed to the injection of charge carriers from the electrode into the PEPC, which establishes a regime in which the current is limited by the space charge.[134] Measurement of the electrical characteristics of the conducting PEPC oligomer and of its complex with tetracyanoquinodimethane (TCQDM) showed that in the region of high potentials the voltage–current characteristics of both the pure oligomer and of its complex are non-linear and exhibit hysteresis. It has been demonstrated by the thermocurrent method that the majority charge carriers in PEPC are electrons, while in the PEPC–TCQDM complex they are holes with concentrations of 8.5×10^{13} and 1.4×10^{14} cm^{-3} respectively.[135] It has been observed that, depending on the conditions in the preparation of the specimen, the real component of the dielectric constant at room temperature is 2.7–3.1 and is associated mainly with electronic polarisation.[138] In layers of the pure EPC oligomer, the tangent of the dielectric losses angle ($\tan\delta$) has a distinct maximum above the glass point; the maximum shifts towards higher temperatures with increase in the molecular weight and with increase in the frequency of the electric field f, the $\tan\delta$ curve becoming broader under these conditions.

The effective activation energy E, obtained from the temperature dependence of the maximum value of $\tan\delta$, amounts to 2.4 eV for the oligomer with $\overline{M}_n$ = 750 and 3.2 eV for PEPC with $\overline{M}_n$ = 1570.[138] The static dielectric constant ε_s of PEPC layers, determined from the Cole–Cole diagram, is 7.84. It has been suggested that ε_s of PEPC layers, like that of PVCA layers,[136] is determined by the polarisation of the carbazole groups.[137]

The dielectric properties and structure of PEPC irradiated with UV light and γ-quanta in the presence of oxygen have been investigated.[139] A significant influence of different types of radiation on the dielectric parameters of PEPC has been observed, which is associated with the structural changes occurring in the polymer.

When PEPC was irradiated with UV light for periods up to 30 min, a sharp decrease in $\tan\delta$ and ε' was observed. With increase in the duration of irradiation, $\tan\delta$ and ε' rise to a maximum and then diminish monotonically until the attainment of a plateau after irradiation for 8 h. The decrease in $\tan\delta$ and ε' in the initial stage of the photochemical process has been explained by a significant contribution of peroxy-radicals, formed during the irradiation process, to the depolarisation of PEPC. The peroxy-radicals, which have a large dipole moment,[140] interact with dipoles and some of the dipoles, whose interaction energy with the charge field is greater than the energy of their interaction with the applied field, are not involved in the relaxation. This diminishes $\tan\delta$ and ε' as a consequence of the decrease in the concentration of the dipoles acting in the relaxation process. The increase in the dielectric parameters has been attributed to the formation of stable carbonyl groups.

The temperature and field dependences of ε' and $\tan\delta$ for layers of pure PEPC and its complex with TNF have been investigated.[141] It has been shown that the character of the temperature dependence of ε' for the PEPC and EPPC–TNF layers is identical but in the complex ε' is somewhat higher than in the pure oligomer, which has been explained by the contribution of the TNF molecule to the polarisation of the system and also by the electronic thermal polarisation due to weakly bound electrons arising in the complex formation process.

The electrical conductivity of films of PEPC and the copolymer of EPC with 5% of BGE (where BGE = butyl glycidyl ether) has been investigated by the method of thermostimulated currents in the Al–PEPC–SnO_2, Al–(EPC + 5% BGE)–SnO_2, and Al–PVB–(EPC + 5% BGE)–SnO_2 sandwich structures (where PVB represents a layer of a dielectric–polyvinylbutyral).[142] It was observed that, in the ranges 213–263 K and $E = 10^7$–10^8 V m^{-1}, a saturation current regime obtains in the PEPC and PEPC + 5% BGE films in which the current varies linearly with the hole generation efficiency within the bulk of the film (having a thermal field character) and with the film thickness, while in the range 273–313 K the electrical conductivity is determined by the generation and drift of ions.

The nature of the dark electrical conductivity of freshly cast and dried PEPC layers has been investigated by the method involving the dark decrease in potential.[143] Measurements were made of the time variation of the capacitance, ε_s, the charging current in long electrisation stages, and the reduction potential of the specimens with the applied potential and on subsequent short-circuiting. The results indicate the operation of several electrical conduction mechanisms in both fresh and stabilised PEPC layers. A two-layer model of the dark electrical conductivity in PEPC, which explains the polarisation phenomena in this material and describes the changes in its properties on stabilisation, has been proposed.

The electrical conductivity of a composition based on PEPC with a filler comprising a triphenylmethylphosphonium–TCQDM radical-ion salt has been investigated.[144] The electrical conductivity of the composition is determined by the contact conductivity at the boundary between the particles of the filler and the binder. The contact conductivity is non-linear and is of the semiconducting type. The activation energy for the electrical conduction in the composition exceeds E_σ for the filler and the binder. It has been suggested that the electrical conduction is effected by the emission of electrons from part of the filler and their activated transport in the layer of the binder.

4. Practical applications of carbazole-containing polymers

The high photoconductivity of carbazole-containing polymers with added organic dyes (OD) and with electron-accepting compounds (EAC) permits their use as photosemiconducting materials for the preparation of electrophotographic layers (EPL) designed for microfilming, the recording of information by the photothermoplastic method, and for the manufacture of multicolour electrophotographic images and slides.[1]

Studies on the possibility of creating EPL and other non-silver layers on the basis of polymeric photoconductors are being widely prosecuted at the present time in the USSR, Japan, the Federal Republic of Germany, the USA, and other countries. Organic compounds belonging to a wide variety of different classes are used as light-sensitive media suitable for electrophotographic processes.[145–148]

Many studies have been devoted to the use in EPL of polymers containing in their structure the carbazole nucleus, for example, polyallylcarbazole, polypropenylcarbazole, poly-*N*-acryloylcarbazole, and their derivatives, as well as 1,4-divinylcarbazole polymers and copolymers.[147] However, PVCA is one of the most thoroughly investigated carbazole-containing polymeric photosemiconductors which is widely used in electrophotography. Oligomeric PVCA is used in the USSR for the manufacture of electrophotographic and photothermoplastic materials.[149–151]

Photothermoplastic layers must be transparent in the visible part of the spectrum and elastic and must have a smooth surface and resistivities in the solid and softened states of $10^{14}-10^{15}$ and $10^{10}-10^{11}$ Ωcm. They must be effectively charged in the dark, must possess thermoplastic properties and a glass point in the range 50–80 °C,[56,152] and must not break on repeated bending and on being immersed in the carrier liquid of the electrophotographic developer and on cooling (to a temperature below –60 °C).[153] In this respect the EPL based on the EPC oligomers[40] are believed to be extremely promising in applications which include the formation of a multicolour electrophotographic image.[154]

Electrophotographic films based on PEPC have been investigated[106] and a detailed study has been made of the photoelectric properties of PEPC and its possible applications have been defined. The sensitisation of PEPC by various electron-accepting compounds and organic dyes has been studied and the most effective sensitisers for this purpose have been discovered. It has been shown that the introduction of electron-accepting compounds and of an organic dye into the PEPC layer alters the conditions in the generation and transport of carriers. PEPC layers sensitised by polynitrofluoroenones are effectively charged, both positively and negatively, and exhibit a weak dark relaxation of the potential and a zero residual potential, while PEPC layers sensitised by organic dyes exhibit a fairly pronounced dark relaxation of the potential.

Organic electrophotographic films (OEPF) of three types have been developed on the basis of PEPC:[153] OEPF-M of type T-1 for the generation of images in accordance with the positive–positive or negative–positive scheme with positive charging, OEPF-M of type T-2 in accordance with the positive–positive scheme with negative charging, and OEPF-M of type T-3 for the preparation of positive images in accordance with the positive–positive (negative charging) or negative–positive (positive charging) scheme. In an OEPF frame, it is possible to form up to eight images and by developing them with different toners it is possible to obtain multicolour images (resolving capacity 300 lines mm^{-1}) which are stable under an illumination of 5×10^4 lx and at a temperature of 55 °C for 24 h.

Panchromatic EPL for colour images have been developed on the basis of PEPC to which 1–15 mol% of TENF has been added.[154] It has been shown that, with increase in the TENF content to 10 mol%, the photosensitivity increases almost linearly. A further increase in the acceptor concentration does not increase the photosensitivity and in the blue region of the spectrum actually reduces it. An increase in the TEMF content leads to a slight diminution of the positive potential in the dark (from 3 to 5%), while the dark decrease in the negative potential is constant and amounts to 6%. The dark decrease in potential rises to 8–10% when the degree of illumination is high (5×10^3 lx in 1 min).

It is known that, when EPL based on PEPC are used under real conditions, the working parameters of the photosemiconductor are influenced by various external factors (UV irradiation, oxygen, temperature, etc.), which lead to photochemical oxidation and other changes. Photochemical oxidation processes can be regarded to some extent as model reactions in relation to the real operating conditions of photothermoplastic materials in electrophotographic and photothermoplastic regimes.

By studying the influence of UV irradiation on the electrophotographic sensitivity (EPS) and diffraction efficiency (DE) of EPL, it is possible to obtain definite information about the characteristics of the degradation of these materials.[78]

The most significant changes in photosensitivity are observed after brief UV irradiation (up to 1 h): there is initially a sharp decrease in the EPS and then a slight increase. The attainment of an EPS plateau as a function of the duration of irradiation is observed for exposures ranging from 1 to 10 h. It has been noted that the character of the variation of EPS during UV irradiation is independent of the type of electron acceptors introduced into the PEPC. Reactions involving carbazole nuclei play the main role in the changes in EPS during photochemical oxidation. Brief UV irradiation does not entail a change in the diffraction efficiency of photothermoplastic carriers (PTC) based on PEPC + 2% TNF. The maximum diffraction efficiency, observed for exposures of 0.1–0.15 mJ cm^{-2} is 20–22% for carriers based on PEPC + 2% TNF and PEPC + 2% CA and 16–18% for PEPC + 5% CA. For carriers with a high TNF concentration (5% and above) and also for DCMTNF (3% and above), holographic recording is hardly feasible.

In the PEPC spectra, the long-wavelength absorption band and the first photosensitivity maximum are determined by the carbazole chromophoric group and are in the UV region of the spectrum at $\lambda = 345$ nm.[119] In order to impart to the organic conductor sensitivity in the visible region of the spectrum, spectral sensitisation by organic dyes or electron-accepting compounds, which form charge-transfer complexes with PEPC, is employed.[106,111,119,122,155]

Table 2. The influence of the nature and concentration of the acceptor on the photosensitivity of PEPC.

Acceptor	Photosensitivity ($E_0 = 75$ V μm^{-1}) at different acceptor concentrations (mol%), 10^3 lx^{-1} s^{-1}					
	0.1	0.5	1.0	2.0	5.0	10.0
9-Fluorenone	0.04	0.045	0.04	0.044	0.04	0.12
DNF	0.08	0.22	0.5	0.5	0.8	2.9
TNF	0.14	0.5	0.8	1.15	2.5	4.2
TENF	0.3	0.6	1.12	3.1	4.0	7.2

The xanthene dye rhodamine 6 G is regarded as a highly effective sensitiser (in relation to electrophotographic sensitivity) of PEPC EPL among organic dyes,[110,111] while among electron-accepting compounds polynitrofluorenones (TNF and TENF) are effective.[106,122]

The dependence of the photosensitivity of PEPC layers on the content of rhodamine 6 G in the layer, shows that the highest photosensitivity is that of PEPC layers containing 0.9 mol% of the dye.[111] At $\lambda = 540$ nm, the photosensitivity of this composition reaches 29 m^2J^{-1}.

Table 2 presents the photosensitivites of positively charged PEPC layers, sensitised by nitrofluorenones, on illumination with white light[122] (DNF = 2,7-dinitrofluorenone).

The decrease in potential in the dark over a period of 1 min at E_0 = 75 V μm^{-1} does not exceed 5%. The absence of the photosensitivity of the unsensitised layers in the presence of a negative charge shows that holes but not electrons are mobile in PEPC. In the PEPC + 1 mol% TNF or TENF compositions, photosensitivity appears also in the presence of a negative charge. At such concentrations of electron-accepting compounds, electrons also become mobile. The introduction of organic dyes and electron-accepting compounds into PEPC results both in an increase in the electrophotographic sensitivity in the intrinsic absorption band of the oligomer and in the expansion of the spectral range of the photosensitivity up to 650 nm.

Measurements have been made of the dependence of the photosensitivity of PEPC layers on the amount of pyrylium salt introduced and the distributions of the spectral sensitivity of the layers in the wavelength range 250–650 nm have been investigated.[119] In order to sensitise PEPC, pyrylium salts with different substituents in the 2-, 4-, and 6-positions in the pyrylium ring, comprising perchlorate and tetrafluoroborate anions, have been studied.

Among the pyrylium salts investigated, the best sensitisers of PEPC layers are 4,6-diphenyl-2-*p*-tolylpyrylium perchlorate (D1), 2,6-dianisyl-4-phenylpyrylium perchlorate (D2), 2,6-dianisylpyrylium perchlorate (D3), 4-anisyl-2,6-dinaphthylpyrylium tetrafluoroborate (E1), 2-anisyl-4,6-diphenylpyrylium tetrafluoroborate (E2), and 2,6-dianisyl-4-phenylpyrylium tetrafluoroborate (E3).

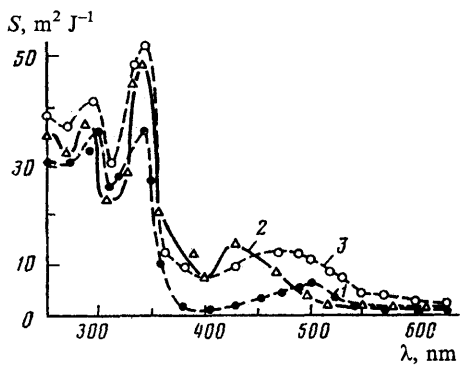


Figure 1. Distribution of the spectral sensitivity (S) of PEPC layers sensitised by the pyrylium salts D3 (curve *1*), D1 (curve *2*), D2 (curve *3*); $E = 5 \times 10^7$ V m^{-1}, c = 1 mol%, positive charge.[119]

The sensitivity of the unsensitised PEPC layers at λ = 295 nm for $E = 5 \times 10^7$ V m^{-1} is about 2 $m^2 J^{-1}$. A small amount of pyrylium salts greatly increases the photosensitivity of PEPC layers. It has been shown that the maximum concentration for the majority of pyrylium salts is 3–5 mol% relative to the PEPC monomeric unit. However, in the presence of 1–3 mol% of the sensitiser, saturation of the photosensitivity is observed and, on further increase in the content of the pyrylium salt, the photosensitivity begins to fall. The decrease in photosensitivity is explained by the formation of a negative space charge which reduces the rate of the photoinduced decrease in the potential.

Figs. 1 and 2 present curves for the distribution of the spectral sensitivity of PEPC layers containing 1 mol% of pyrylium salts. It is seen from the figures that pyrylium salts having a long-wavelength absorption maximum in the visible part of the spectrum have a much higher sensitising effectiveness than polynitrofluorenones and rhodamine 6G.

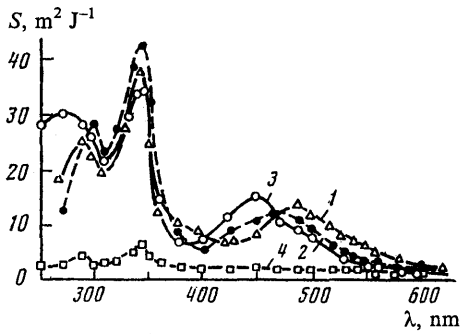


Figure 2. Distribution of the spectral sensitivity (S) of PEPC layers sensitised by pyrylium salts E3 (curve *1*), E2 (curve *2*), and E1 (curve *3*) (c = 1 mol%) and by TNF (curve *4*) (c = 3 mol%); $E = 5 \times 10^7$ V m^{-1}, positive charge.[119]

It is known that low-molecular-weight impurities, polymer end groups, triplet oxygen, polymer oxidation and photochemical oxidation products, and specific local conformations of the macromolecules can serve as deep centres for the capture of mobile holes in carbazole-containing photosemiconductors.[156–158] Low-molecular-weight ionogenic impurities can influence the visualisation of a latent electrophotographic image in the electrophotographic layer, which results in the appearance of different defects and in the diffuseness of information symbols on the developed image. The conditions in the synthesis of PEPC influence significantly the residual potential (U_{res}) of its electrophotographic layer. The main cause of the high value of U_{res} in PEPC layers is traces of the anionic catalyst and of electron-donating substances with a lower ionisation potential than that of the carbazole chromophore.[118,157]

The study of the photosensitivity and U_{res} of PEPC specimens obtained by anionic and cationic polymerisation and sensitised by TNF and 2,4,6-triphenylpyrylium perchlorate, introduced in amounts of 0.5 and 3 mol% respectively and 0.1 and 0.5 mol% respectively into a monomeric unit of the oligomer, showed that PEPC specimens with a low U_{res} are sensitised more effectively in both the UV and visible parts of the spectrum.[157] The residual potassium hydroxide decomposes the pyrylium sensitisers in the PEPC layers.

At the present time, the PEPC used for the preparation of electrophotographic layers is obtained by the anionic polymerisation of EPC in the presence of potassium hydroxide followed by treatment of the product with acetic acid.[157] In order to reduce U_{res}, the PEPC should be carefully freed from technological impurities, including the catalyst, before the preparation of the electrophotographic layer.

Electrophotographic layers based on industrial PEPC, purified by adsorption, chromatographic, and ion-exchange methods, have been investigated.[158] It has been shown that the greatest decrease in the residual potential of the PEPC electrophotographic layer is obtained when solutions of PEPC in polar solvents are treated with activated charcoal and by passing its solutions through layers of Al_2O_3 or silica gel.

The development of electrophotography imposes stringent requirements on the electrophotographic microfilming apparatus for the representation and replication of information. This suggests the use of semiconducting systems with improved electrophotographic properties.[159]

One of the ways of improving electrophotographic properties of layers based on PEPC is its chemical modification.[89]

In order to prepare layers with an improved electrophotographic sensitivity, brominated PEPC, sensitised by TNF and pyrylium salts, can be used as the photosemiconductor. Brominated PEPC layers sensitised by TNF and pyrylium salts are more photosensitive than the analogous PEPC layers.[89,120,121] This is especially appreciable in the case where PEPC is sensitised by pyrylium salts. The pyrylium cation, which has an exceptionally high electron affinity, ensures electron transfer over long distances from bromocarbazolyl to the pyrylium salt, which leads to an appreciable separation of the charges of the ion pair and to effective dissociation of the electron donor–electron acceptor complex in the electric field with formation of a mobile hole.

The characteristic features and the mechanism of the dark charging processes[160–164] and photocharging processes[165–169] involving pure and sensitised PEPC electrophotographic layers have been investigated. The influence of luminescence on the latent electrophotographic image[170,171] and also of prolonged illumination on the optical, photoelectric, and thermomechanical properties of electrophotographic information carriers (EPIC), prepared on the basis of PEPC,[172] have been investigated. As a result of photochemical reactions, on irradiation with UV light the absorption by electrophotographic information carriers increases in the visible region, the photosensitivity falls, and the rate of discharge in the dark increases. Owing to the impairment of thermomechanical properties, cracking on bending is then observed which precludes photothermoplastic recording. The removal from the spectrum of the UV lamp of radiation at wavelengths less than 400 nm makes it possible to eliminate effects associated with the light-induced ageing of electrophotographic information carriers.

PEPC layers with added TNF have been used to prepare photoelectric converters[173,174] and a varistor.[175] On illumination of a "sandwich" cell with a photosensitive PEPC layer to which 0.5–3.0 wt.% of TNF had been added by light from an incandescent lamp, a photo-e.m.f. equal to 0.6 V was generated between the electrodes for an incident light energy of 20 mW cm^{-2}.[174] The short-circuit photocurrent was in the range 0.1–0.5 μA cm^{-2}. The elucidation of the nature of the photo-e.m.f., in particular the character of the transitions at the aluminium–photoconductor and photoconductor–aquadag contact as well as the estimation of the yield of the diffusion photo-e.m.f. (Dember's e.m.f.) requires further studies. The data obtained have shown that the photovoltaic effect is sufficiently large to suggest that PEPC is a promising material for the manufacture of photocells based on it.

The photocells based on PEPC[173,174] and PVCA[176,177] known at the present time have low efficiencies but their appreciable increase may be expected when the optimum metallic electrode–polymer combination has been selected and also after the development of a technology for the preparation of ultrathin uniform films with a high electrical conductivity.

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The study of the polymerisation of epoxypropylcarbazoles in the presence of various catalysts indicates its very effective occurrence under the influence of anionic catalysts. The use of potassium hydroxide as the catalyst is apparently most suitable as regards the technological aspects of the process. In view of the favourable disposition of carbazole side substituents and the presence of ether linkages in the main chain, EPC oligomers have effective physicochemical and photoelectric properties which permit their use in electrophotography and also in the thermoplastic recording of information.

The basic data on the electrical, optical, dielectric, and photovoltaic properties of carbazole-containing polymers and charge-transfer complexes have now been obtained. Electrophotographic layers used for microfilming, photothermoplastic devices, and the recording of information have now been produced on the basis of carbazole-containing polymers and their derivatives with different acceptors. Studies in this field are extremely promising and are being prosecuted in many world laboratories. The first polymeric photocells based on carbazole-containing polymers have already been created, although they still have low efficiencies. However, the simplicity of their preparation and the low cost of the initial materials have stimulated the development of research into the synthesis of new photoconducting polymers in order to manufacture highly efficient photoelectric cells.

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