Translated from *Uspekhi Khimii*, 54, 1175-1207 (1985) U.D.C. 541.64

The Synthesis and Luminescence-spectroscopic Properties of Fluorescent Condensation Polymers

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The results of studies on the synthesis of polycondensation phosphor-containing aliphatic and aromatic polymers as well as the products of polymer-analogue transformations with phosphor-groups in the side chain are examined. The light absorption and luminescent properties of the polymers obtained and of model compounds having an analogous structure are discussed. The bibliography includes 108 references.

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I. INTRODUCTION

Numerous studies on the synthesis and spectroscopic properties of fluorescent polymers have been published in recent years. However, the available results have not so far been the subject of a suitable survey in the Soviet literature. Foreign reviews deal only with data on the synthesis and spectroscopic properties of polymerisation phosphor-containing polymers.[1-3] Nevertheless the knowledge of the luminescence-spectroscopic properties of such polymers, obtained both by polymerisation and polycondensation, is of great theoretical importance in view of the possibility of investigating intramolecular and intermolecular electronic energy transfer and migration processes in a polymeric medium and is of definite practical interest, because the fluorescent properties of polymers are closely related to their photoconducting characteristics and resistance to the action of light.

In recent years a number of trends have arisen in technology which utilise the capacity of certain polymers for intense fluorescence. These include in the first place the preparation of daylight fluorescent pigments on a polymeric base and of plastic scintillators[4] as well as polymeric active elements for laser technology.[5]

In the present review an attempt is made to survey the available literature data on the synthesis and spectroscopic characteristics of aliphatic and aromatic phosphor-containing condensation polymers.

II. ALIPHATIC POLYCONDENSATION POLYMERS

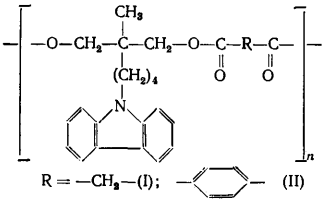
It is known[6-8] that many of the natural polycondensation polymers (proteins) glow in the range 280–360 nm as a result of the emission of light by aromatic aminoacid residues—those of tryptophan, tyrosine, and phenylalanine. Synthetic polycondensation polymers [of the type of polycaprolactam and poly(ethylene terephthalate) containing chromophoric groups in the chain], which have a bright colour and apparently fluoresce, were first obtained by Bykov and co-workers at the beginning of the 1960's.[9-12] Data obtained in these and similar investigations have been surveyed in a review.[13]

Concentrating on later investigations, we may note that the ability of polycondensation polymers to fluoresce has been usually imparted by introducing into the composition phosphor fragments related to carbazole, anthracene, pyrene, or other condensed aromatic or heteroaromatic nuclei. We shall consider polymers of each of these types.

1. Carbazole-Containing Polymers

Carbazole-containing polymers, obtained by polarisation methods, in particular polyvinylcarbazole, are promising materials for electrophotography, which is based on the phenomenon of the photoeffect in electrically charged high-resistance films.[14] Cheap electrophotographic layers, whose sensitivity is close to those made from inorganic photoconductors, can be obtained on the basis of such polymers.[15] According to Voishchev et al,[16] certain polycondensation carbazole-containing polymers, which have been described in fair detail in the literature,[17] also exhibit a high photoconductivity. However, the luminescence-spectroscopic properties of such materials have been investigated less fully than those of polyvinylcarbazole and related compounds.[1] Thus the synthesis of fluorescent polyesters[18-20] and polyurethanes[21] with ω-9-carbazolylbutyl groups, as well as polyamides based on 3,6-diamino-9-ethylcarbazole[22] has been described in a series of reports by Tazuke and co-workers.

The polyesters (I) and (II) have been obtained by the polycondensation of 6-carbazolyl-2,2-dihydroxymethylhexane with the diethyl esters of dicarboxylic acids at 150–160 °C for 3 h in a nitrogen atmosphere and then *in vacuo* for 10 h:[18,19]



The light absorption and fluorescent properties of the polymers (I) and (II) have been investigated simultaneously with the properties of the model compound (III) (Fig.1), which is a product of the condensation of 6-carbazolyl-2,2-dihydroxymethylhexane with ethyl acetate. Fig.1*a* shows that the absorption properties of the polymers (I) and (II) are similar in the range $\lambda > 270$ nm, where the only

light absorbing group is the carbazolyl group. The differences in the range $\lambda < 270$ nm are associated with absorption by the terephthalate unit. The fluorescence spectra of the polyester (I) and of the model compound (III) are identical and contain only the monomer fluorescence band with $\lambda_{max} = 368$ nm. On the other hand, an additional broad structureless exciplex band with $\lambda_{max} = 490$ nm appears in the fluorescence spectrum of the polyester (II). The intensity ratio of the exciplex and monomer fluorescence bands† I_e/I_m depends on the degree of polycondensation n[19] and diminishes when the solution is diluted. The latter finding indicates the operation of an intermolecular mechanism of the formation of the exciplex even at a concentration of 10^{-4} M.[18]

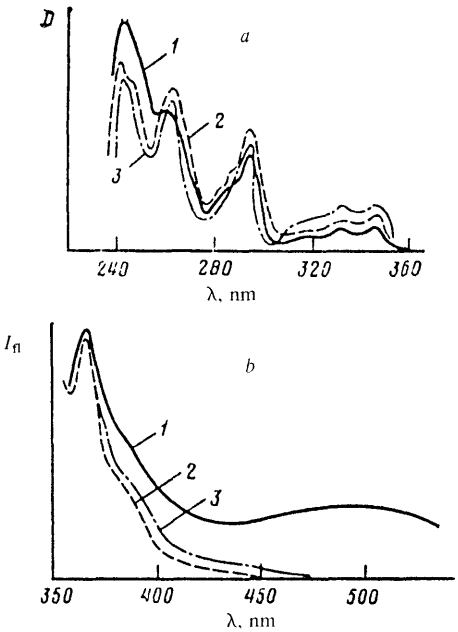
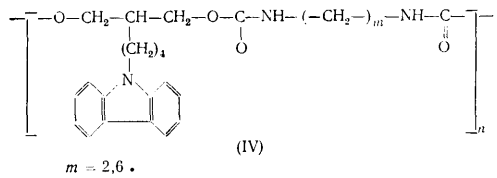


Figure 1. Absorption (*a*) and fluorescence (*b*) spectra of dioxan solutions of the polymers (II) (curve *1*) and (I) (curve *2*) and the model compound (III) (curve *3*).[18]

It follows from the fluorescence quantum yields for the polyester (I) and the model (III) (~0.3) and for the polyester (II) (less than 0.1) that the probability of the fluorescence of the exciplex formed as a result of the interaction of the excited carbazolyl group of the model (III) with a terephthalate group is lower than for the carbazolyl group. Comparison of the fluorescence lifetimes of compounds (I), (II), and (III) justifies the hypothesis that the reduced fluorescence intensity of the carbazolyl groups of the polyester (II) is due to the dynamic quenching of the fluorescence by terephthalate groups.

A method has been proposed[21] for the synthesis of carbazole-containing polyurethanes involving the polycondensation of 9-(6-hydroxy-5-hydroxymethylhexyl)-carbazole with aliphatic di-isocyanates in boiling anisole:

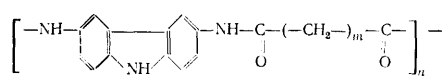


(IV)

$m = 2,6$.

The spectroscopic properties of the polymers (IV) and (I) are similar, i.e. are determined mainly by the carbazole chromophore without an admixture of exciplex states.

The polyamides (V), containing carbazole groups in the main chain and not in the side chain, have been obtained by the polycondensation of 3,6-diamino-9-ethylcarbazole with aliphatic dicarboxylic acid dichlorides in 9-ethylcarbazole using triethylamine as the catalyst:[22]



V

$m = 2, 6, 8$.

The fluorescent properties of the polymers (V) and of the model compound 9-ethyl-3,6-bis(propionylamino)carbazole have been investigated in solutions in hexane and *m*-cresol. It is shown that solutions of both compounds are characterised by the same monomeric fluorescence without a contribution due to the glow of excimers. The significant bathochromic shift of the fluorescence band, observed for the solution in *m*-cresol ($\lambda_{max} = 410$ nm) is explained by the authors by the formation of a hydrogen bond between the OH group of the solvent and the amide bond in the test substances.

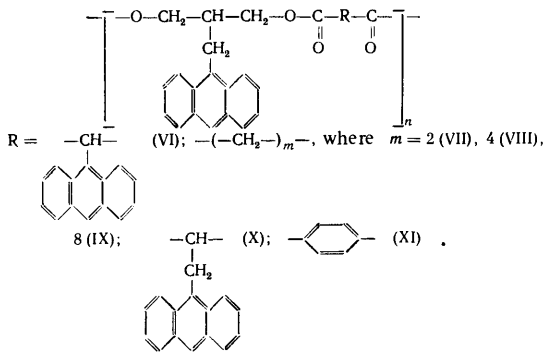
2. Anthracene-Containing Polymers

It is known[23] that anthracene-containing polymerisation systems of the type of poly-9-vinylanthracene belong to the class of photosemiconductors, which are promising for the preparation of electrophotographic layers. Presumably polycondensation polymers with anthracene fragments in the side chain will also be of interest as photoconducting materials. However, all the available literature data on such polymers deal primarily with questions of electronic energy transfer in these systems and with the observation of excimer glow and not with their photoconducting characteristics.

Among anthracene-containing polycondensation polymers, one should distinguish polyesters,[24-28] polyurethanes,[26-28] and polymeric quaternary ammonium salts (polyionenes).[29-31]

In order to obtain the polyesters (VI)–(XI), 2-(9-anthryl)-methylpropane-1,3-diol was subjected to polycondensation with dicarboxylic acid esters at 150–160 °C in the presence of catalytic amounts of calcium acetate and antimony trioxide:[24]

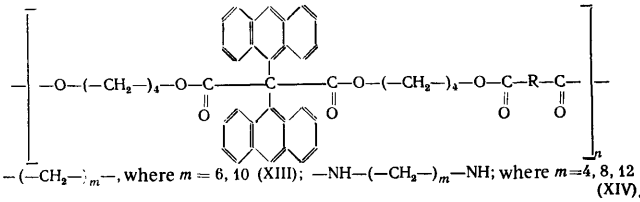
†Here and henceforth monomer fluorescence should be understood as the emission associated exclusively with the nature of the individual chromophoric polymer fragments, while the excimer and exciplex fluorescence should be understood as the emission by complexes consisting respectively of two identical or different molecules, one of which is in the ground state, while the other is in an excited state.



The polymers synthesised are soluble in tetrahydrofuran (THF) and, according to gel-permeation chromatographic data, have a low molecular weight (n = 2–7). The polyesters (VII), (IX), and (XI) were also synthesised by the reaction of the initial propanediol with the dithiol esters of the corresponding dicarboxylic acid at 150–160 °C for 2–3 h in an atmosphere of nitrogen and then *in vacuo* for 13–18 h in order to remove the thiophenol.[25] This method made it possible to obtain polyesters with higher molecular weights (n = 4–25).

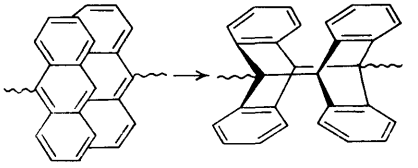
A study of the luminescence-spectroscopic properties of solutions and films of polymers as well as solutions of the model 1,3-diacetoxy-2-(9-anthryl)methylpropane (XII) showed that the light absorption properties of all the substances investigated are similar. The fluorescence spectra of solutions of the polymers contain both monomer bands with λ_{max} = 392, 415, and 440 mn as well as bands due to excimer glow with λ_{max} = 460 nm (Fig.2). It was found that the ratio I_e/I_m for the polymer solutions falls from 0.431 to 0.024 in the series of compounds (VI) > (X) > (VII) > (VIII) > (IX) > (XI). In the polymer films the excimer fluorescence predominates over the monomer fluorescence (Fig.2*b*). The fact that the polyester (VI) has the most intense excimer fluorescence is apparently associated with the high efficiency of the energy transfer in this polymer. A study of the dependence of I_e/I_m on the content of the polymer (VI) in solution showed that the interaction between the anthryl units predominates at a concentration $\leqslant 10^{-3}$ M (I_e/I_m = const.), while at higher concentrations the contribution of intermolecular interactions increases (I_e/I_m increases with increasing concentration). The occurrence of energy transfer process between various phosphor units has been demonstrated in relation to the polyester (X): on excitation of fluorescence with light having λ = 280 nm, which is absorbed by naphthyl groups, emission from the anthryl units alone was observed (Fig.2*b*).

A method has been proposed[26,27] for the synthesis of the polyester (XIII) and the polyesterurethanes (XIV) by the polycondensation of 9,10-bis-4-(hydroxybutylenoxycarbonyl)dianthracene with acid dichlorides or di-isocyanates:



The polymers obtained are readily soluble in chloroform and methylene chloride and have comparatively high molecular weights.

It has been shown[27] that, when the polymers (XIII) and (XIV) are irradiated with light at a wavelength of 300 nm at 196 K, a small fraction (up to 5%) of the dianthracene units are photolysed to anthroate groups:



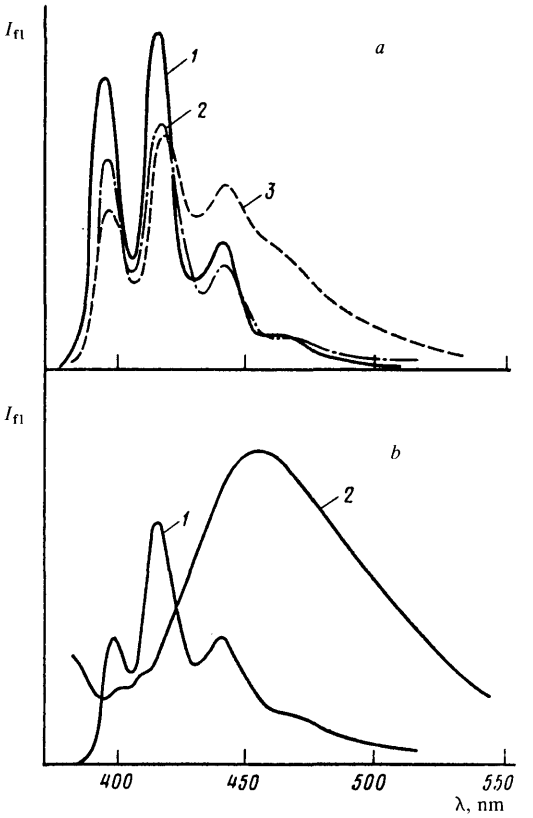
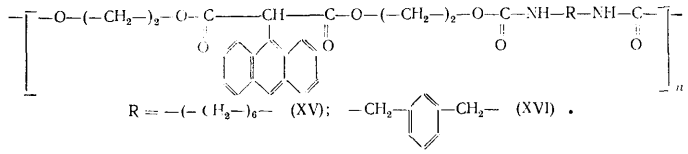


Figure 2. Fluorescence spectra: *a*) of solutions in THF of the model compound (XII) (curve *1*), the polyester (X) (curve *2*), and the polyester (VI) (curve *3*); *b*) of a solution of the polyester (VIII) in THF (curve *1*) and of a film of the polyester (VII) (curve *2*).[24]

The anthroate end groups are formed as sandwich dimers, which gradually decompose to the monomeric state on heating.[27] The formation of dimers is indicated by a broad structureless band with a maximum at 500 nm in the fluorescence spectra of the polymers after photolysis at 196 K. In the specimens of polyesterurethanes (XIV) the structure of the sandwich dimers is retained at 20 °C, while in the polyesters (XIII) these complexes are stable only at low temperatures. The fluorescence spectra of the isolated anthroate end groups show that the rotational mobility of

the phosphor units in the polymer (XIV) is lower than in (XIII). The restricted mobility of these groups influences the formation of new dianthracene units on irradiation with light at the wavelength corresponding to the ^1L_a absorption band of the anthroate group.

The anthracene-containing polyurethanes (XV) and (XVI) were obtained[28] by the interaction of bis(2-hydroxyethyl)-9-anthrylmethyl malonate and the corresponding di-isocyanates in anisole for 6 h:



R = —(—CH_2—)$_6$— (XV); —CH_2—⟨⟩—CH_2— (XVI).

The polymers (XV) and (XVI) are soluble in THF and have molecular weights ranging from 4100 to 11000 according to gel-permeation chromatographic data.

Fig.3 presents the absorption and emission spectra of polyurethane (XV) films. The broad absorption bands at 360 and 380 nm are apparently associated with the presence of sandwich dimers, which are formed as a result of the close spacing of the anthryl groups parallel to one another. The fluorescence spectra of solutions of the polymers (XV) and (XVI) in THF correspond to transitions involving the emission from both monomeric units and excimers. The fluorescence excitation spectra of the polymer films are broader than the analogous spectra of the solutions, which indicates an appreciable role of the interaction between the macromolecules in the solid specimen.

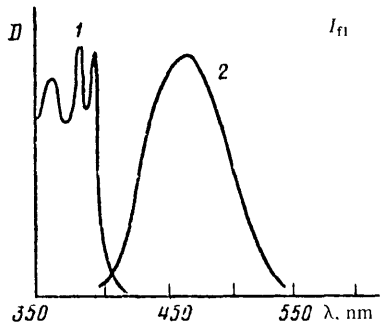
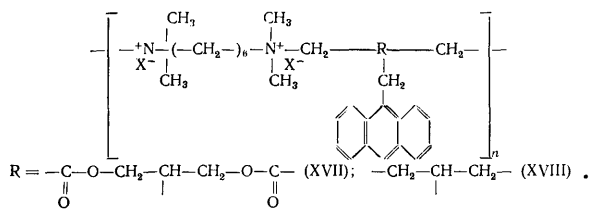


Figure 3. Absorption (curve *1*) and emission (curve *2*) spectra of a film of the polyurethane (XV).[28]

The light absorption and fluorescence properties of the polyionenes obtained by the Menshutkin reaction involving the interaction of 1,3-bis[halogenoacetoxy-2(9-anthryl)-methylpropane] or 2-[(9-anthryl)methyl]trimethylene halides with tertiary diamines have been described in a series of communications:[29-31]



R = —C(=O)—O—CH_2—CH(—CH_2—O—C(=O)—)— (XVII); —CH_2—CH(—CH_2—)— (XVIII).

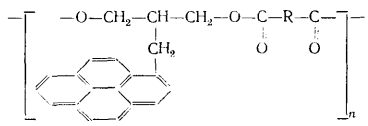
The polymers (XVII) and (XVIII) were synthesised in dimethylformamide, dimethylacetamide, dimethyl sulphoxide, or sulpholan at 40–60 °C over periods of 20–126 h.

Like other polymers with a similar structure,[15] the polyionenes obtained are apparently capable of forming conducting radical-ion salts with powerful electron acceptors (of the type of tetracyanoquinodimethane). The presence of the electron-donating anthryl groups in the polymers should have a favourable effect on the electrophysical characteristics of these systems.

The study of the fluorescent properties of the polyionenes (XVII) and (XVIII) showed that the formation of hydrophobic domains in aqueous solutions due to the anthrylmethyl groups, which are responsible for the appearance of a broad structureless excimer emission band with a maximum at 500 nm, is characteristic of these substances. The addition of methanol to solutions of the polymers promotes the decomposition of the hydrophobic domains and diminishes the intensity of the excimer fluorescence. On the other hand, the addition of electrolytes intensifies the excimer glow and this effect is greater the higher the ionic strength of the solution.

3. Pyrene-Containing and Other Polycondensation Polymers

Tazuke and co-workers considered the synthesis of a series of pyrene-containing polyesters based on monomers of the type of 3-pyrenylpropane-1,3-diol.[25,32-35] The use for this purpose of the reaction of the diol with dithiol esters of dicarboxylic acids at 150–170 °C initially in an inert atmosphere and then *in vacuo* made it possible to obtain the polymers (XIX) with molecular weights higher by a factor of 2–5 than in the traditional polycondensation of diols with acid dichlorides:[25,35]



R = —(—CH_2—)$_m$—, where m = 2, 4, 8, 10 (XIX); ⟨⟩—CH—CH_2—⟨⟩—$N(CH_3)_2$ (XXI)

The light absorption properties of the polyesters (XIX) are independent of the nature of the acid residue and are similar to the properties of the model compound (XX)—the product of the acylation of 3-pyrenylpropane-1,3-diol (λ_{max} = 344 nm). On the other hand, in the fluorescent properties of these systems there are differences (Fig.4) associated with the appearance of the exciplex glow (λ_{max} = 480–490 nm) in the case of the polymer.

The emission spectra of the polymers (XIX) are close to those of other pyrene-containing polyesters (XXI) with dimethylaniline side groups.[32-34] The latter were synthesised by the bulk polycondensation of the corresponding propanediol with diethyl 4-(*NN*-dimethylamino)benzyl malonate in the presence of calcium acetate as the catalyst at 160–210 °C *in vacuo*.

Polymers similar to the polyester (XXI) and containing electron-donating (*NN*-dimethylaniline) and electron-accepting (pyrenyl) groups are of interest from the standpoint of the formation of charge-transfer complexes, which as a rule exhibit an enhanced photosensitivity over a wide spectral range.[15,23]

The absorption and fluorescence spectra of solutions of the model compound (XX) and of the polyester (XXI) are compared in Fig.4*b*. Comparison of the absorption spectra of the polymer and the model indicates a weak interaction between the chromophores in the ground state. It was

found[32] that the ratio of the intensities of the exciplex fluorescence with λ_{max} = 498 nm and of the monomer fluorescence with λ_{max} = 377 nm increases with increasing concentration of the polymer solution and the character of the relation is determined by the nature of the solvent. Whereas in an effective solvent (dichloroethane) the relation $I_e/I_m = f(c)$ is linear, in a poor solvent (mesitylene) it tends to saturation. The authors concluded[32] that in mesitylene the intermolecular formation of the exciplexes reaches saturation at an early stage, while in dichloroethane their formation is facilitated by "allosteric" association in which the macromolecules are arranged relative to one another in such a way that the electron-accepting fragments of one of them adjoin the electron-donating fragments of another without disturbing the conformation of the polymer as a whole. Association of this kind is particularly favourable for macromolecules with a moderate molecular weight. Indeed the $I_e/I_m = f(n)$ relation for the polyesters (XXI), in which the degree of polycondensation n is controlled and varies from 1 to 18, passes through a maximum at n = 14 (in dichloroethane) and n = 7 (in mesitylene).[33]

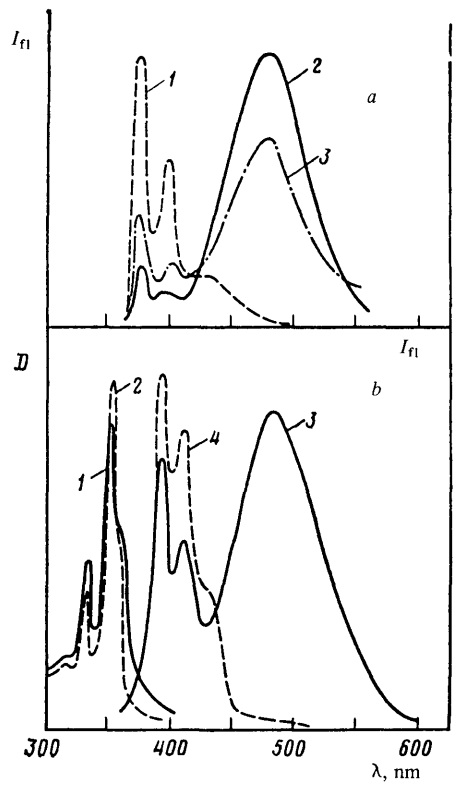
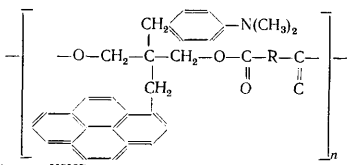


Figure 4. *a*) Emission spectra of solutions in THF of the model compound (XX) (curve *1*) and the polymer (XIX) with R = $-(CH_2)_2-$ (curve *2*) and $-(CH_2)_{10}-$ (curve *3*); *b*) absorption spectra (curves *1* and *2*) of solutions in 1,2-dichloroethane and emission spectra (curves *3* and *4*) of solutions in dioxan of the model compound (XX) (curves *2* and *4*) and the polymer (XXI) (curves *1* and *3*).[32]

Together with intermolecular complex formation, intramolecular association also makes some contribution to the formation of exciplexes. This has been confirmed by the observation[33] that the model compound containing both the dimethylaniline and pyrenyl fragments exhibits an appreciable exciplex fluorescence regardless of the concentration of the solution. On the other hand, a solution of a mixture of two model compounds, each of which contains one of the above groups, does not exhibit an exciplex glow.

It has been shown[34] that the role of the intramolecular interactions in the polyesters (XXI) becomes dominant when the temperature is reduced to 77 K. In this case the band with λ_{max} = 498 nm disappears from the fluorescence spectra of the polymers and a new band appears with λ_{max} = 440 nm, which has been attributed to the emission of an electron donor–electron acceptor complex. Its formation is confirmed by the broadening of the band in the absorption spectra of solutions of the polymer (XXI) relative to the spectra of the model compounds. In contrast to the glow of the exciplexes, the intensity of the fluorescence of the donor–acceptor complexes increases with increasing molecular weight of the polymer and with decrease of temperature and is almost independent of the polymer concentration in solution.

The polyesters (XXII), which also contain the pyrene and dimethylaniline groups, but, in contrast to the polymers (XXI), these are attached to a single carbon atom, have been investigated:[35]



R = $-(-CH_2-)_m-$ (XXII); $-NH-(-CH_2-)_m-NH-$ (XXIV), where m=2–10.

Measurement of the fluorescence spectra of the polyesters (XXII) and of the model compound (XXIII)—the acylated 2-(4-*NN*-dimethylaminobenzyl)-2-(1-pyrenylmethyl)propane-1,3-diol—in solution in THF demonstrated the presence of a weak band with λ_{max} = 380 nm in the region corresponding to emission from the monomeric pyrene units and of intense exciplex fluorescence with λ_{max} = 520 nm.

Comparison of the emission spectroscopic data for the polymers (XXI) and (XXII) shows that the mutual approach of the electron-donating and electron-accepting fragments entails a bathochromic shift of the exciplex fluorescence. The authors emphasise[35] that the exciplex bands in the fluorescence spectra of solutions of the polyesters (XXII) and the model compound (XXIII) have different forms. The difference is apparently caused by the fact that only the intramolecular interaction of the donor with the acceptor occurs in solutions of the model compound at a concentration less than 10^{-5} M, while in the case of polymers both intramolecular and intermolecular interactions take place.

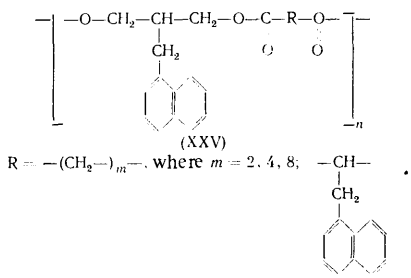
Other polymers with pyrenyl and dimethylaniline groups, namely the polyurethanes (XXIV), have been described.[36] They were synthesised by the interaction of 2-(4-*NN*-dimethylaminobenzyl)-2-(1-pyrenylmethyl)propane-1,3-diol with di-isocyanates in anisole at 150–160 °C in the presence of triethylamine as the catalyst.

The study of the fluorescence characteristic of solutions of the polymers (XXIV) showed that the position of the exciplex fluorescence maximum is in the range from 485 to 505 nm and depends significantly on the molecular weight of the polymer and its concentration in solution. The ratio I_e/I_m increases with increasing concentration in the intermediate range of molecular weights, which indicates the association of the macromolecules in solution. Comparison of the spectra of polymers in which the number of methylene

groups in the di-isocyanate residue is 6 and 8 demonstrated convincingly that even small changes in the structure of the polymers (XXIV) and hence in the rigidity of the polymer chain have an appreciable influence on the intermolecular and intramolecular formation of exciplexes and the fluorescence properties of the polymer.

Apart from the polymeric system with pyrenyl fragments examined above, polycondensation polymers with phosphor units of the naphthalene,[37-40] *p*-phenylenediacrylic,[41,42] 3-methoxybenzanthrone,[43] and naphthalimide[44] types are known.

Polyesters with the naphthylmethyl side groups (XXV) have been synthesised by the polycondensation of 2-[(1-naphthyl)-methyl]propane-1,3-diol with the diethyl esters of dicarboxylic acids at 150–160 °C for 3 h in an inert atmosphere and then *in vacuo* for 10 h:[37]



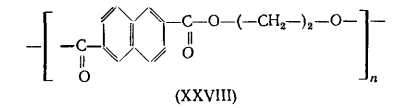
(XXV)

R = $-(CH_2-)_m-$, where $m = 2, 4, 8$; $-CH-$ with CH_2 and a naphthyl group

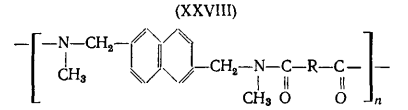
According to gel-permeation chromatographic data, the polymers have a low molecular weight (n = 3–10).

The study of the fluorescence properties of the polymers (XXV) was preceded by the investigation of model compounds—1,3-bisacetoxy-2-(1-naphthyl)methylpropane (XXVI) and di[3-(1-naphthyl)propyl]adipate (XXVII). It was found that, in contrast to the emission spectra of the model compound (XXVI), those of solutions of the polymers (XXV) contain, together with the monomeric fluorescence band having λ_{max} = 324 nm, also a broad excimer band with λ_{max} = 400 nm. The intramolecular formation of excimers takes place even in those cases where the naphthyl groups are separated by 16 carbon atoms and two oxygen atoms. The ratio I_e/I_m for the polymeric system (XXV) is higher that for the corresponding dimeric system (XXVII). The authors[37] explain this by the fact that the local concentration of the naphthyl units in the ground state in the vicinity of the excited group, considered in isolation, is higher in the polymer macromolecule than in the dimeric system.

The fluorescence properties of naphthalene-containing polymers of another type, namely the polyesters (XXVIII) and polyamides (XXIX) with naphthalene nuclei bound directly in the main polymer chain, have been described:[38,39]



(XXVIII)



(XXIX)

R = $-(-CH_2-)_m-$, where $m = 2, 4, 6, 8$.

Comparison of the fluorescence properties of the polyesters (XXV) and (XXVIII) shows that the introduction of the naphthalene fragments into the main polymer chain induces a bathochromic shift of the monomer and excimer glow. The ratio of the intensities of the excimer (λ_{max} = 420 nm) and monomer (λ_{max} = 370 and 385 nm) fluorescence of solutions of the polymer (XXVIII) in chloroform increases by a factor of 3 when its concentration rises from 0.024 to 43 dl g^{-1} and, on passing to solid films, the increase is by a factor greater than 6 (compared with the minimum concentration in solution). The same type of dependence of I_e/I_m on the polymer concentration in solution has been observed also for the phenyl-containing polyester.[39] However, in the case of the polyester (XXVIII) one observed the formation of intramolecular excimers, which fluoresce even in very dilute solutions, and this is apparently associated with the longer lifetime of the excited states of the naphthyl chromophores. This is valid also for other types of naphthalene-containing polymers.[1]

We shall consider the formation of fluorescent intermolecular charge-transfer complexes in relation to the polyamide (XXIX).[38] We may note that the only complete review of studies on such complexes has been published recently.[40]

Fig.5 presents the fluorescence spectra of dilute solutions of the polyamide (XXIX) (m = 4) in methylene chloride in the presence and absence of a low-molecular weight electron donor (triethylamine). Evidently, when triethylamine is added to the polyamide, the intensity of the intrinsic fluorescence of the polymer, with a maximum at 360 nm, diminishes and a broad exciplex fluorescence band appears with a maximum at 500 nm. A linear relation has been found between the concentration of triethylamine and the ratio I_e/I_m. It has been shown that tendency towards the formation of exciplexes diminishes in the series of polyamides with decrease of m in the acid residue, i.e. in parallel with increasing steric restriction of the mobility of the naphthyl groups.

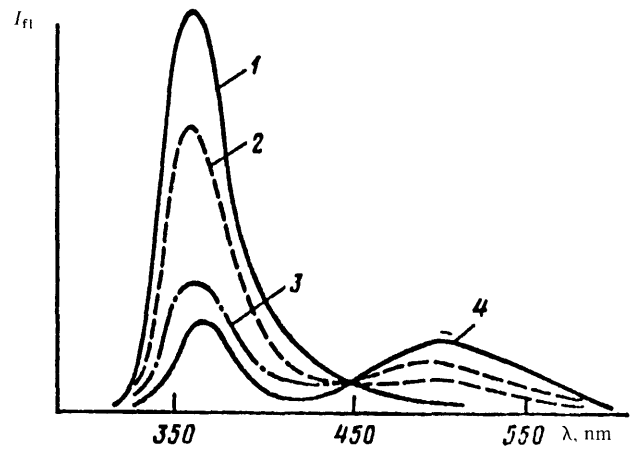
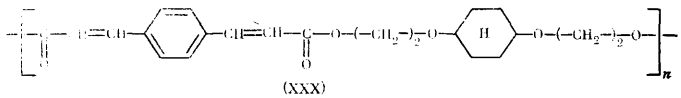


Figure 5. Fluorescence spectra of solutions of the polyamide (XXIX) (m = 4) in methylene chloride in the absence of triethylamine (curve *1*) and in the presence of various concentrations of triethylamine (M): *2*) 0.01; *3*) 0.06; *4*) 0.19.[38]

An industrial photoconducting polymer (XXX), used for the preparation of printing plates and obtained from *p*-phenylenediacrylic acid and 1,4-bis(2-hydroxyethoxy)-cyclohexane, has been investigated from the standpoint of its fluorescence properties:[41,42]



(XXX)

At the same time a study was made of the fluorescence characteristics of the model compound (XXXI), namely the diethyl ester of *p*-phenylenediacrylic acid. Fig.6, which presents the emission spectra of these two systems, shows that those of solutions of the model compound and the polymer (XXX) contain short-wavelength monomer fluorescence bands with a maximum at 370 nm and a longer-wavelength broad band due to the excimer glow, the intensity ratio of these bands depending on the concentration of the solution. The spectrum of a film of the polymer shows only the excimer fluorescence with a maximum at 470 nm.

It has been shown[41] that the kinetics of the decay of the glow in the region of 470 nm can be fitted by the sum of two exponential functions; the short-lived fluorescence is due to the monomer, but the long-lived fluorescence is due to the excimers. The lifetime of the long-lived fluorescence diminishes with increasing concentration of the phenylene diacrylate groups, which indicates a bimolecular character of the decay of the excimer glow. It has been found that the excimers are formed on excitation of pairs of chromophores already present in solution before excitation.

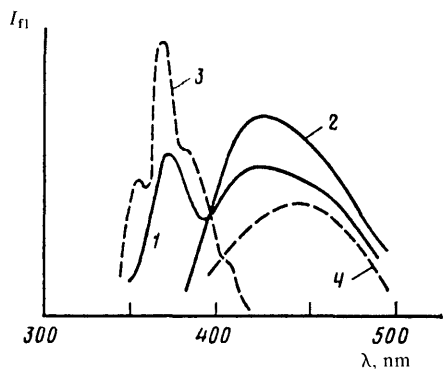


Figure 6. Emission spectra of dilute solutions of the polymer (XXX) (curve *1*) and the model compound (XXXI) (curve *3*) in 1,2-dichloroethane, of a film of the polymer (XXX) (curve *2*), and of a concentrated solution of the polymer (XXXI) (curve *4*).[41]

The melaminotoluene-*p*-sulphonamideformaldehyde (MTSF) resins, which are frequently used as the polymer base for the preparation of daylight fluorescent pigments,[4] can be classified as an aliphatic polycondensation polymer. The phosphor containing a reactive group is added in the synthesis stage of the MTSF resins, which consists in heating a mixture of toluene-*p*-sulphonamide, melamine, and formaldehyde; the resulting polymer is chemically bound to the phosphor molecule. The chloromethyl, hydroxymethyl, carboxy, anhydride, or amino-groups can be used as the reactive groups of this kind, while 3-methoxybenzanthrone residues[43] and derivatives of 1,8-naphthalic acid[4,44] can serve as the phosphor fragments.

Analysis of the available data on the synthesis and spectroscopic properties of fluorescent polycondensation polymers permits the conclusion that those whose phosphor fragments were introduced into the macromolecule via the diamine (diol) component and not via the acid component have been most thoroughly investigated. The phosphor groups are mainly responsible for the long-wavelength absorption and fluorescence characteristics of the polymers and the emission spectra can show both the monomer bands and the excimer (exciplex) fluorescent bands. The tendency towards the formation of exciplexes increases appreciably when the macromolecule contains fragments capable of intramolecular and intermolecular donor–acceptor interaction.

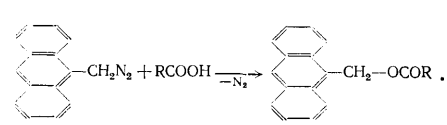
III. PRODUCTS OF POLYMER-ANALOGUE TRANSFORMATIONS

The first fluorescent polymers obtained by the method of polymer-analogue transformations have been proteins coloured by active luminescent dyes. A condition for the covalent binding of these dyes to proteins having SH, OH, and H_2N side groups is the presence in them of reactive groups of the type of SO_2Cl, N=C=O, and N=C=S. Derivatives of naphthalene, anthracene, fluorescein, rhodamine, and a number of others are used to dye proteins.[45]

The study of protein macromolecules labelled with luminescent dyes makes it possible to investigate the properties of electronically excited states and the specific features of the electronic transitions in such systems and enables one to follow the kinetics of the structural and physicochemical transformations of proteins.[46] Furthermore, the purely analytical use of the luminescence for the determination of the protein in biological preparations is of considerable interest.[4]

Some of the early investigations of macromolecules with phosphor side groups were those of Wahl,[47,48] who described the interaction of polymers containing amino-groups (of the type of polyvinylamine, poly-*p*-aminostyrene, and polyethyleneimine) with 1-dimethylaminonaphthalenesulphonyl chloride. The reaction was carried out by mixing an aqueous solution of the polymer with a solution of the sulphonyl chloride in acetone. Depending on the reactant ratio, fluorescent polymers with different numbers of naphthalene groups in the side chain are formed.

Later the luminescent units were introduced into the side chains of polymers by the reaction of their carboxy-groups[49–53,55] (see also Metaga and Kubota[54]), the acid chloride groups,[56] hydroxy-groups,[57–61] or benzene rings.[51,62] The interaction of polymeric acids of the type of polyacrylic and polymethacrylic acids or their copolymers with phosphors such as 9-anthryldiazomethane, 9-methyl-10-anthryldiazomethane, or diazomethyl α-naphthyl ketone has been investigated.[49–51] The reaction was carried out both in a homogeneous medium (methanol) and in immiscible solvents (water–hexane) at 20–55 °C:

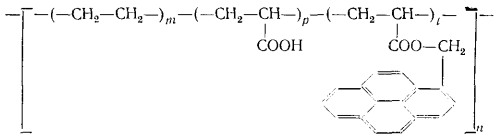


The concentration of the fluorescent groups introduced can be varied within wide limits by altering the polymer : diazomethane ratio. The fluorescence properties of the resulting polymers were similar to those of the model 9-anthrylacetoxymethane. Monomer fluorescence without an admixture

of the glow due to excimers is characteristic of both types of compounds. The study of polymers labelled with anthracene fragments made it possible to employ the method of polarised luminescence[63,64] for the investigation of the relaxation phenomena in solutions of macromolecules (intramolecular and intermolecular interactions, structure formation, gel formation, etc.).

The interaction between 9-anthryldiazomethane and the copolymers of styrene with acrylic, methacrylic, and vinylbenzoic acids followed by spectrophotometric measurements on the reaction product in the range 390–410 nm has been suggested for the analytical determination of the content of carboxy-groups in these polymers.[50]

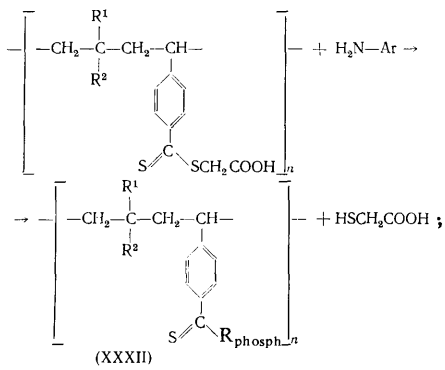
Polymeric styrene-containing sensitisers (XXXI), which are of interest for the preparation of photosensitive layers, have been obtained[53] from a radiation-modified polyethylene containing 45–47% of grafted COOH groups. Compound (XXXI) was synthesised by the reaction of the modified polyethylene with 1-hydroxymethylpyrene in THF or acetonitrile at 60 °C in the presence of dicyclohexylcarbodiimide as the catalyst.



(XXXI)

The study of the fluorescence properties of films of the polymers (XXXI) with different degrees of esterification showed that the intensity of the excimer fluorescence with λ_{max} = 465 nm increases as the concentration of the pyrene groups rises.

A number of interesting coloured polymers exhibiting a weak fluorescence have been described.[52] They were obtained by the reaction of polyethylene-4-thiobenzoylthio-2-acetic acid or the copolymers of the initial thioester with styrene, methyl methacrylate, or methacrylic acid and diamines of the type of Acridine Yellow, 1-aminoanthraquinone, and Cresol Blue:



(XXXII)

$R^1 = C_6H_5$, $R^2 = H$; $R^1 = CH_3$, $R^2 = COOH$ or $COOCH_3$; R_{phosph} = phosphor residue.

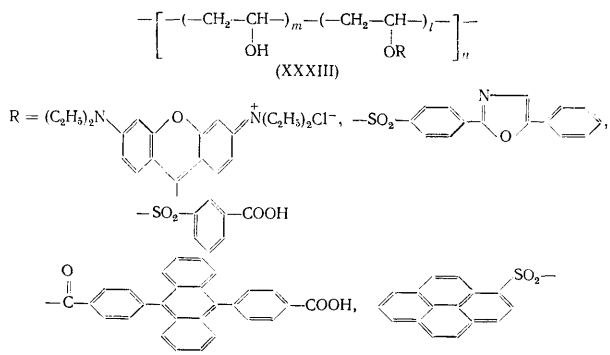
The reaction is carried out in a 1:1 dimethylformamide–benzene mixture with a polymer:amine ratio of 2:1 for 24 h at room temperature. The fluorescence properties of the copolymers (XXXII) were not investigated in detail. It was only noted that the intensity of the glow of the initial dyes, for example, of Acridine Yellow, diminishes appreciably after binding to the polymer. The authors[52] do not give any explanation of the observed phenomenon. In our view its possible cause is the formation of hydrogen bonds between the diaminoacridine fragment and the hydrogen donor present in the system, namely thioglycolic acid, which promotes the quenching of the fluorescence according to Mataga and Kubota.[54]

Whereas the carboxy-groups of the polymers have been used in a number of studies[49–53] to form strong covalent bonds with the fluorescent molecule, in the systems described by Fenyo[55] the bond linking polyacrylic and polymethacrylic acids to the phosphor amine is salt like. Fenyo's aim[55] was to investigate the conformational behaviour of the macromolecule in solution. Compounds which the authors chose as the amines were auramine, which does not dimerise and exhibits a weak fluorescence, and 9-aminoacridine hydrochloride, which is capable of forming dimers and exhibits an intense fluorescence. It has been shown that the binding of the dye is determined by three factors: the nature and conformational state of the polyions (the degree of ionisation α), the polymer:dye molar ratio, and the ionic strength of the solution. The intensity of the emission by auramine increases by a factor of 100 in the presence of poly(methacrylic acids). An increase of the fluorescence quantum yield and of the relative content of the bound dye with increasing polymer:dye ratio has been observed for this compound.

An increase in the degree of ionisation of the polymeric acid diminishes the efficiency of the binding of the dye to the polymer in the case of auramine and, conversely, leads to its increase in the case of 9-aminoacridine hydrochloride. Furthermore, it has been observed that, for low values of α, the addition of poly(methacrylic acids) to the last phosphor diminishes the intensity of its fluorescence. Fenyo[55] put forward an explanation of the observed differences in the behaviour of the phosphors on the basis of a comparison of the rigidities of the skeletons of their molecules and the presence of side groups in the latter.

We shall now proceed to the polymer-analogue transformations of hydroxylated polymers. Fluorescein isothiocyanate has been used[57] as reagent with the OH groups of a constituent of starch, namely amylose having a molecular weight of 1700. The fluorescence lifetimes of the resulting polymer were measured at different concentrations and pH of the solutions.

The luminescence-spectroscopic properties of films and solutions of poly(vinyl alcohol) (XXXIII), containing four types of phosphors as side groups, namely diphenyloxadiazole, diphenylanthracene, rhodamine B, and pyrene, have been investigated:[58–60]



(XXXIII)

The polymers (XXXIII) were synthesised by treating poly(vinyl alcohol) with the corresponding sulphonyl chloride or acid chloride in *N*-methylpyrrolidinone, initially at room temperature and then at 60–70 °C. Depending on the ratio of the initial reactants, polymers containing from 5 to 10 phosphor fragments per 1000 elementary units were obtained.

The polymers (XXXIII) exhibit an intense fluorescence and are highly soluble in water, which permits their use as luminescent probes in the study of biological membranes.[63] The polymeric structure of these probes determines their enhanced selectivity in relation to individual cell components as compared with low-molecular-weight phosphors.

Fig.7 presents the absorption and emission spectra of specimens of the first three types of polymers (XXXIII) in the form of thin films. Their comparison with the spectra of the initial phosphor monomers[4] demonstrates their similarity. The similarity of the fluorescence characteristics of the polymers to those of the corresponding low-molecular-weight compounds confirms the monomer character of the emission without an appreciable contribution by excimer states. The same conclusion can be reached on the basis of a comparison of the emission spectra of solutions of these systems.

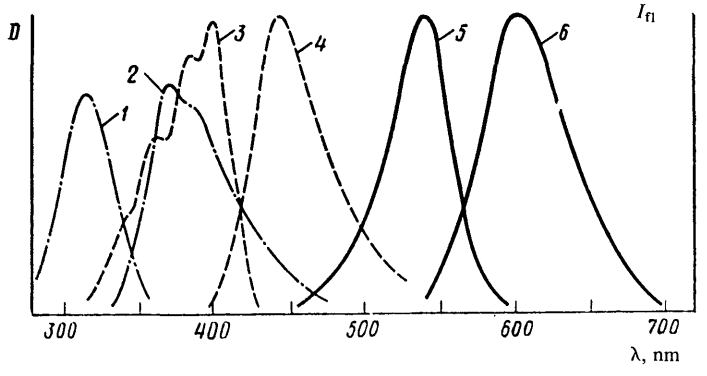
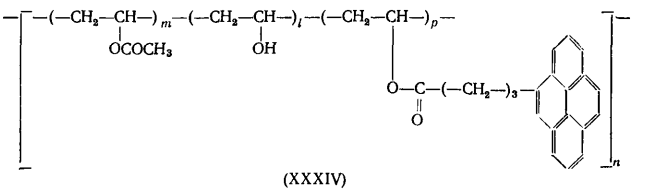


Figure 7. Absorption (curves *1*, *3*, and *5*) and fluorescence (curves *2*, *4*, and *6*) spectra of films of the polymers (XXXIII) containing diphenyloxazole (curves *1* and *2*) diphenylanthracene (curves *3* and *4*), and rhodamine B (curves *5* and *6*) units in the side chain.[60]

The fluorescence spectra of the pyrene-containing polymers (XXXIII) are more complex (Fig.8). Evidently, depending on the concentration of the solution, either only monomer fluorescence bands due to the pyrene groups with λ_{max} = 376, 395, and 415 nm are present in the spectra or they are accompanied by the excimer band with λ_{max} = 495 nm. The authors[59,60] observed a direct linear relation between the ratio I_e/I_m and the concentration of an aqueous solution of the polymer (XXXIII). When water was replaced by a more viscous solvent (ethylene glycol) a sharp decrease of the intensity of the excimer glow was observed, while the intensity of the monomer fluorescence bands was unchanged. Evidently the increased viscosity of the solvent diminishes the rate constant for the intramolecular formation of excimers, which agrees with a diffusion-controlled mechanism.

The latter conclusion has also been confirmed by the results of Cuniberti and Perico,[61] who investigated a partly hydrolysed poly(vinyl acetate) (XXXIV) treated with 4-(3-pyrenyl)butyric acid in THF in the presence of trifluoroacetic anhydride at 50 °C. This method made it possible to obtain a polymer with an average spacing between the pyrenyl groups equivalent to approximately 200 units:



(XXXIV)

It follows from the fluorescence spectra of solutions of the polymer (XXXIV) in methanol and ethylene glycol that both a monomer emission with λ_{max} = 396 nm and an excimer emission with λ_{max} = 480 nm are observed in the former solvent. In the more viscous ethylene glycol the excimer fluorescence is absent. A dependence of the ratio I_e/I_m on the viscosity of the medium has been observed for mixtures of solvents of similar types.[61]

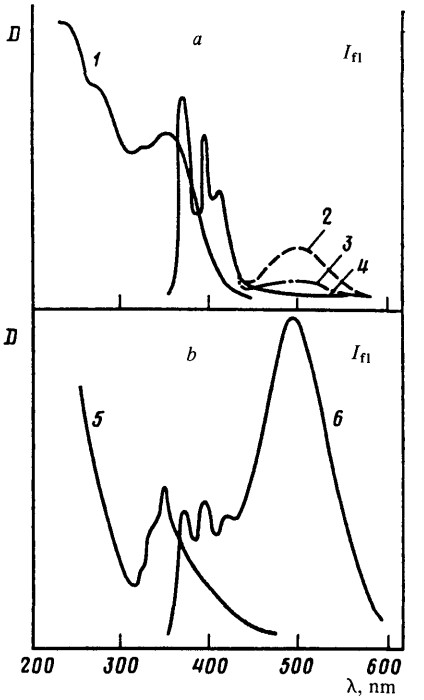
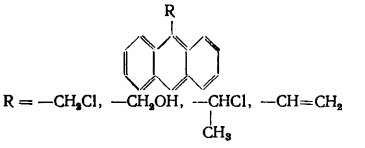


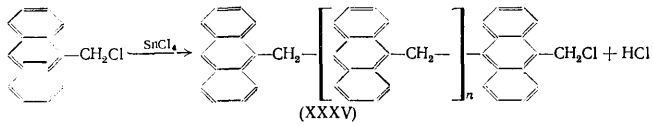
Figure 8. Absorption (curves *1* and *5*) and fluorescence (curves *2*, *3*, *4*, and *6*) spectra: *a*) of aqueous solutions of the pyrene-containing polymer (XXXIII) at concentrations of 0.28 M (curve *2*), 0.14 M (curve *3*), and 0.017 M (curves *1* and *4*); *b*) of a film of the polymer (XXXIII) (curves *5* and *6*).[60]

The Friedel–Crafts reaction of anthracene derivatives with the benzene rings of the macromolecules proved to be a fairly convenient method of synthesis of fluorescent polymers by polymer-analogue transformation.[51,62] It has been suggested that derivatives of the type



be used as the anthracene compounds. Their reaction with phenyl-containing polymers of the polystyrene, poly-α-methylstyrene, poly(benzyl vinyl ether), or poly(benzyl propenyl ether) was carried out at room temperature or at −78 °C for 0.5–360 h using $SnCl_4$ or boron trifluoride as the catalysts.[62] The polymers formed contain from 0.2 to 83 anthracene groups per 1000 polymer units and possess fluorescence properties close to those of the model benzylanthracene (the bands in the fluorescence spectrum of a solution in toluene at λ_{max} = 395, 425, and 440 nm).

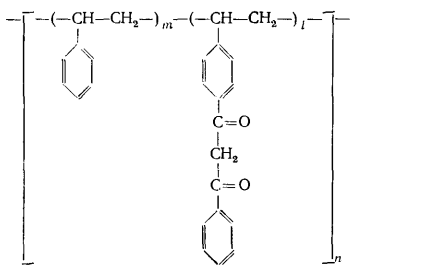
It was shown[62] that polycondensation processes occur simultaneously with alkylation under the conditions of the Friedel–Crafts reaction:



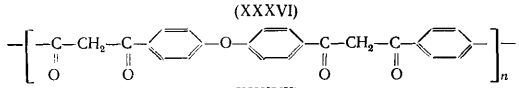
(XXXV)

Thus in the absence of the phenyl-containing polymer, the homopolycondensation of 9-chloromethylanthracene gives rise to the polymer (XXXV) MW = 1500) in 85% yield, the fluorescence spectrum of its solution in toluene containing a short-wavelength band at λ_{max} = 420 nm and a long-wavelength band at λ_{max} = 445 nm, which slowly descends to 560 nm. Homopolycondensation reduces the yield of the alkylation reaction and can lead to the addition of groups of the type of (XXXV) to the phenyl-containing polymer, which is reflected in the fluorescence spectra.

Extremely interesting fluorescent polymers, the method of synthesis of which can also be regarded as approximately polymer-analogue transformations, have been described.[65] These compounds are chelate europium complexes of macromolecules containing β-diketone units as ligands: poly-*p*-benzoylstyrene (XXXVI) and polyaryl-β-diketone (XXXVII):



(XXXVI)



(XXXVII)

The polymers (XXXVI) were synthesised by the reaction of partly acetylated styrene with methyl benzoate in the presence of sodium amide in THF at 50 °C. The europium(III) complexes were obtained by mixing 1–2% solutions of the polymers in THF with a solution of europium trichloride in a THF–methanol mixture.

The interest in the polymeric complexes of the lanthanides is associated primarily with their intense monochromatic fluorescence. This property makes it possible to employ such complexes as the active media in laser technology, their operating characteristics being in a number of instances superior to those of traditional materials for analogous purposes.[5]

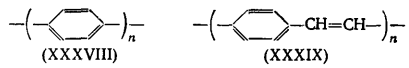
The chelate complexes of the polymers (XXXVI) and (XXXVII) are thermally stable but begin to decompose at 350 °C. The structure of the chelates has been investigated by infrared spectroscopy. It has been noted that the infrared spectrum of the polymer (XXXVII) has in the main an enolic structure with a broad absorption band in the region of 1350–1600 cm^{-1}.[65] When a chelate ring with Eu^{3+} is formed, a new intense band, corresponding to the asymmetric and symmetric vibrations of the C=O bonds and having a resonance structure appears in the spectrum at 1400–1530 cm^{-1}. The Eu^{3+} ions involved in complexes with the polymers (XXXVI) and (XXXVII) undergo radiative deactivation on excitation with light in the range of frequencies characteristic of inorganic crystals. The fluorescence spectra of the complexes contain two bands: one with a maximum at 613 nm, due to the $^5D_0 \rightarrow {}^7F_2$ transition, and the other, low-intensity band with a maximum at 580 nm, associated with the forbidden transition $^5D_0 \rightarrow {}^7F_0$. The intensity of the first fluorescence band of the complexes derived from the polymer (XXXVI) increases linearly with increase of the Eu^{3+} concentration to 3 wt.% and then remains constant. These complexes exhibit a fluorescence which is 20–30 times more intense that that of the complexes with the polymer (XXXVII) (containing 1% of Eu^{3+}). The authors[65] believe that this is due to the fact that, when the β-diketone groups are incorporated in the polymer chain, the formation of complex coordinate bonds between the Eu atoms and the β-diketone may be hindered by steric restrictions and by the decrease in the number of rotational degrees of freedom.

Since the fluorescent macromolecules arising in polymer-analogue transformations are in most cases polymers obtained by polymerisation methods, the rules governing their luminescence-spectroscopic properties are those noted in a review.[1] In the case of polymers the processes involving the transfer and migration of energy from the sites where it is absorbed to the sections of the macromolecule where the proximity and parallel arrangement of the planes of the chromophoric fragments promote the formation of excimers take place more or less effectively. A consequence of these processes is the presence in the fluorescence spectra of the polymers, together with the monomer emission band whose position and character are determined primarily by the nature of the chromophore, also of one or several excimer emission bands. In those cases where the absence of excimer emission may be regarded as proved, there is a great likelihood that no electronic excitation energy migration takes place along the polymer chain. One of the possible causes of the low capacity of such polymers for the formation of excimers is the increased flexibility of the macrochains, which disturbs the required planarity in the arrangement of the chromophores.

IV. AROMATIC FLUORESCENT POLYMERS

1. Carbochain Polymers

Aromatic carbochain polymers have been thoroughly investigated from the standpoint of light absorption properties, but their fluorescent characteristics have been investigated to a much lesser extent. An empirical rule established for linear polyenes and poly-*p*-phenylenes[66] (XXXVIII) is valid also for poly-*p*-xylidenes (XXXIX):[67]



(XXXVIII) (XXXIX)

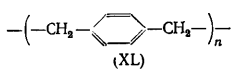
It states that, with increase in the length of the conjugated chain, the energy of the light quantum required for the excitation of the π-electron system diminishes and a bathochromic shift of the long-wavelength absorption band is

observed; after the chain has attained a specific length, the bathochromic shift ceases.[68,69] This shows that the fragment of the macromolecule which behaves as the chromophoric group is consistent with the model in which the number of conjugated π-bonds is less than the number equivalent to the length of the polymer chain. The chromophoric group of the polymer (XXXIX) is approximately equivalent to 3–4 elementary units of the macromolecule.[67]

The fluorescence properties of the polymers (XXXVIII) and (XXXIX) have been investigated.[70,71] A bathochromic shift of the fluorescence band has been observed for the poly-*p*-phenylene (XXXVIII) as its concentration in solution increases, without an appreciable change in the form of the absorption spectra,[70] which is associated with the major role of the energy transfer processes, whose intensity grows as the concentration of the solution rises. At concentrations above 10^{-3} M the energy transfer becomes so effective that quenching of the fluorescence is observed. The study of the effect of quenching agents such as tetracyanoethylene, chloranil, trinitrobenzene, dimethylamine, aminostyrene, and triethylamine on the luminescence of solutions of poly-*p*-phenylene (XXXVIII) showed that, when the absorption spectrum of the quenching agent overlaps the emission spectrum of the polymer, the quenching of the fluorescence can be accounted for by the Forster dipole–dipole energy transfer mechanism. This phenomenon occurs when chloranil is used as the quenching agent. On the other hand, when the absorption spectrum of the quenching agent and the emission spectrum with the polymer do not overlap, then the quenching takes place via a mechanism involving the migration of energy over a short distance or via the formation of donor–acceptor complexes. The latter occurs when aminostyrene, dimethylamine, or triethylamine are used as the quenching agents.

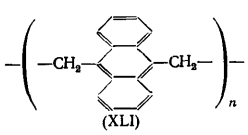
The study of the electronic absorption and emission spectra of polyphenylenes permits a detailed analysis of the mechanism of photoconduction in these polymers.[72]

The light absorption and luminescence properties of polymers with one or two methylene groups between the aromatic rings have been studied.[73–77] The electronic absorption spectra of poly-*p*-xylylene (XL) are characterised by a low-intensity band in the range 260–280 nm:[73,74]



(XL)

The phosphor-containing polymers of the type of poly-9,10-dimethyleneanthracene (XLI), obtained by the pyrolysis of 9,10-dichloromethylanthracene via the stage involving the formation of 9,10-anthraquinodimethane as an intermediate, are of more interest from the standpoint of optical properties:[75]



(XLI)

Fig.9 presents the absorption spectra of the initial 9,10-dichloromethylanthracene at 20 °C, of 9,10-anthraquinodimethane at −196 °C, and of the polymer (XLI) at 20 °C. Evidently the bands in the range 330–420 nm, which are characteristic of the anthracene nucleus, vanish almost completely on passing from 9,10-dichloromethylanthracene to 9,10-anthraquinodimethane. The spectrum of the latter contains only an intense band in the range 270–290 nm associated with the absorption by the anthraquinodimethane chromophore. As this compound is heated from −196 °C to room temperature, the intense absorption band at 291 nm disappears and a band with a maximum at 260 nm as well as a series of bands in the range 330–430 nm appear, confirming the structure of the polymer (XLI) formed.

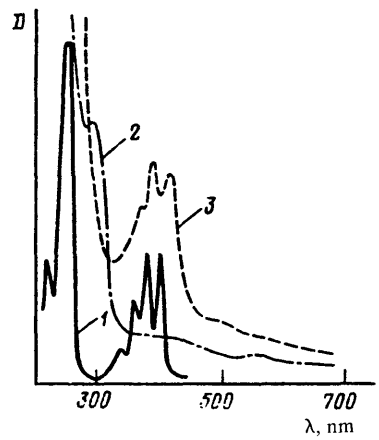


Figure 9. Absorption spectra of a solution of 9,10-dichloromethylanthracene in n-heptane at 20 °C (curve *1*), of 9,10-anthraquinodimethane deposited on a support at −196 °C (curve *2*), and of the polymer (XLI) on a support at 20 °C (curve 3).[75]

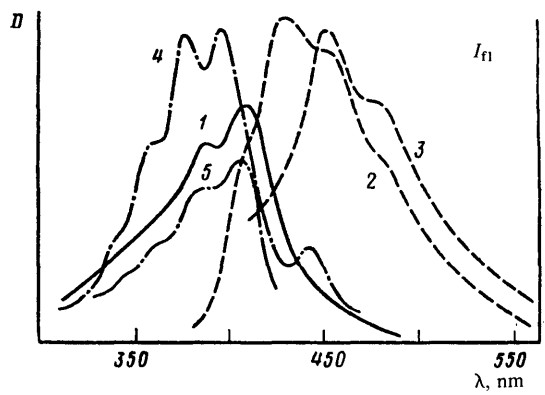


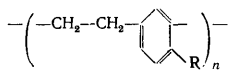
Figure 10. Electronic spectra of a solution of the polymer (XLI) in dimethylformamide: *1*) absorption spectrum; *2*) and *3*) fluorescence spectra (λ_{exc} = 365 and 412 nm respectively); *4*) and *5*) fluorescence excitation spectra for maxima at 432 and 482 nm respectively.[75]

It has been shown[75] that the solid polymer (XLI) does not fluoresce, while its solutions in DMF are characterised by an intense fluorescence. Fig.10 presents the absorption and fluorescence spectra of solutions of the polymer (XLI)

as well as the fluorescence excitation spectra for λ_{max} = 432 and 482 nm. The dependence of the type of the emission spectrum of the solution on the wavelength of the exciting light indicates the presence of two luminescence centres, which is confirmed by the parameters of the fluorescence excitation spectra. It has been suggested[75] that a short-wavelength luminescence centre with λ_{max} = 432 nm is typical of the polymer (XLI). The long-wavelength luminescence centre with λ_{max} = 482 nm is apparently associated either with the presence in the test solution of polymeric associated species or with the presence of low-molecular-weight admixtures of the type of dianthrylethylene derivatives.[4]

The absence of an appreciable fluorescence of the solid phase can also be explained by the admixture of dianthrylethylenes. A characteristic feature of the molecular structure of dianthrylethylene is that they consist of open chains in which there is steric hindrance to the conjugation of π-electron systems or "overlap zones".[78] The presence of such zones significantly diminishes the intensity of the fluorescence of certain dianthrylethylenes compared with the other anthracene derivatives.

Polymers with two methylene groups between the benzene rings in compound (XLII) have been investigated by absorption and luminescence spectroscopy:[76,77]



(XLII)

They have been synthesised by the reaction of 1,2-dichloroethane with substituted benzenes in the presence of $AlCl_3$ as the catalyst.[79] It has been observed that, together with the band at 260 nm corresponding to the π–π* electronic transition in the benzene ring, the absorption spectra also contain bands in the range 300–400 nm, reflecting the vibronic interaction between the ring and the substituent, as well as the bands in the range 450–500 nm due to intermolecular interaction. It has been observed[76] that the intensity of the π–π* transition in these polymers is determined by the excitation vector, whose magnitude depends on the nature of the substituent R.

Summarising the data on the electronic and vibrational absorption spectra of polyarylenealkyls,[80] the author concludes that, as a consequence of intramolecular and intermolecular interactions, a many-centre type of bond arises in the polymers (XLII). According to the existing ideas,[81] the interpretation of the observed EPR absorption signal in these polymers cannot be accepted as correct and the EPR signal is apparently due to the presence of paramagnetic impurities in the polymer. In view of the foregoing, the author's conclusion[76] that the structure of the polymers (XLII) is intermediate between the conjugated and non-conjugated types also appears to be incorrect.

Kozyreva's study[77] was devoted to the observation of the low-temperature luminescence of the polymers (XLII) in the solid phase and in solutions. The phosphorescence of these compounds has been noted, the decrease of the luminescence intensity during the first instants after the removal of the light source being described by a relation of the hyperbolic and then exponential type. On the basis of data which in our view require revision, the author[77] classifies the polymers (XLII) as crystalline phosphors in terms of the type of their luminescence and suggests that they exist in the liquid crystal state at low temperatures.

Thus the observed spectroscopic properties of polyarylenealkyls are as yet not entirely reliable and require revision. Overall, one should note that the available literature data for the luminescence-spectroscopic properties of carbochain aromatic polymers are fragmentary and require further investigations.

2. Heterochain Aromatic Polymers

The optical properties of heterochain aromatic polymers have been studied in greater detail than the properties of the carbochain polymers. There are literature data obtained in investigations of the luminescence-spectroscopic characteristics of aromatic polyethers,[82] poly-Schiff bases,[83–85] polyamides,[86–89] and polyureas.[86,90]

The study of polyoxy-(2,6-dimethyl)-1,4-phenylene by luminescence spectroscopy showed[82] that it exhibits an intrinsic fluorescence in the form of solutions and films in the ultraviolet region (λ_{max} = 320 nm) and an impurity luminescence in the visible part of the spectrum (λ_{max} = 550 nm), the intensity of the latter diminishing on photolysis of the polymer.

The luminescence-spectroscopic properties of poly-Schiff bases and of model compounds have been investigated by D'Alelio et al[83] and by Vasilenko and co-workers.[84,85] In their studies of the absorption and fluorescence spectra of arylazomethines, Vasilenko and co-workers[84,85] observed that protonation imparts to their molecules a planar configuration and hence diminishes the probability of the radiationless deactivation of the S_1 state. It has been shown[91,92] that the fluorescence process in the free bases of arylazomethines is suppressed by the radiationless internal conversion, whose rate constant has been estimated as 10^{12} s^{-1} for *N*-benzylideneaniline. After comparing the absorption spectra of the hydrocarbon and sulphuric acid solutions of *N*-benzylideneaniline, Vasilenko and co-workers[84,85] concluded that in the protonated form of this molecule the π-electrons are strongly bound and are excluded from the π-electron system of the arylazomethine, as a consequence of which the long-wavelength band in the spectrum of the acid solution undergoes a 25 nm bathochromic shift.

Continuing their investigation of the luminescence-spectroscopic properties of arylazomethines in relation to poly-Schiff bases and a number of model compounds such as the product of the condensation of *m*-phenylenediamine with isophthalic aldehyde [compound (XLIII)] or benzaldehyde [compound (XLIV)] and also the product of the condensation of *p*-phenylenediamine with terephthalic aldehyde [compound (XLV)] or cinnamaldehyde [compound (XLVI)], Vasilenko and co-workers[84,85] observed that the characteristic features of the optical behaviour of *N*-benzylideneaniline discovered in various media persist on passing to more complex systems (Fig.11*a*). Evidently in the case of the solution in sulphuric acid the absorption spectra of the polymer (XLIII) and the model (XLIV) are similar (λ_{max} = 340 nm for the long-wavelength band), whereas for the solution of compound (XLIV) in a non-polar solvent (cyclohexane) λ_{max} = 330 nm.[85] Consequently both the polymers and low-molecular-weight bis(arylazomethine) derivatives are protonated at the nitrogen atoms in sulphuric acid, like *N*-benzylideneaniline, which activates the fluorescence of the test systems.

Fig.11*a* shows that the fluorescence spectra of compounds (XLIII) and (XLIV) are similar and have a resolved vibrational structure with 1300–1000 cm^{-1} gaps between the bands. Analogous conclusions can be reached from the analysis of the absorption and low-temperature fluorescence spectra of the polymer (XLV) and the model (XLVI) (Fig.11*b*). Comparison of the spectra in Figs.11*a* and 11*b* shows that, on passing from the *m*-isomers of the polymeric and model arylazomethines to the *p*-isomers, the long-wavelength

absorption band and all the bands in the fluorescence spectrum are seen to undergo a bathochromic shift; the luminescence intensity of the powdered polymer specimens increases in the same sequence.

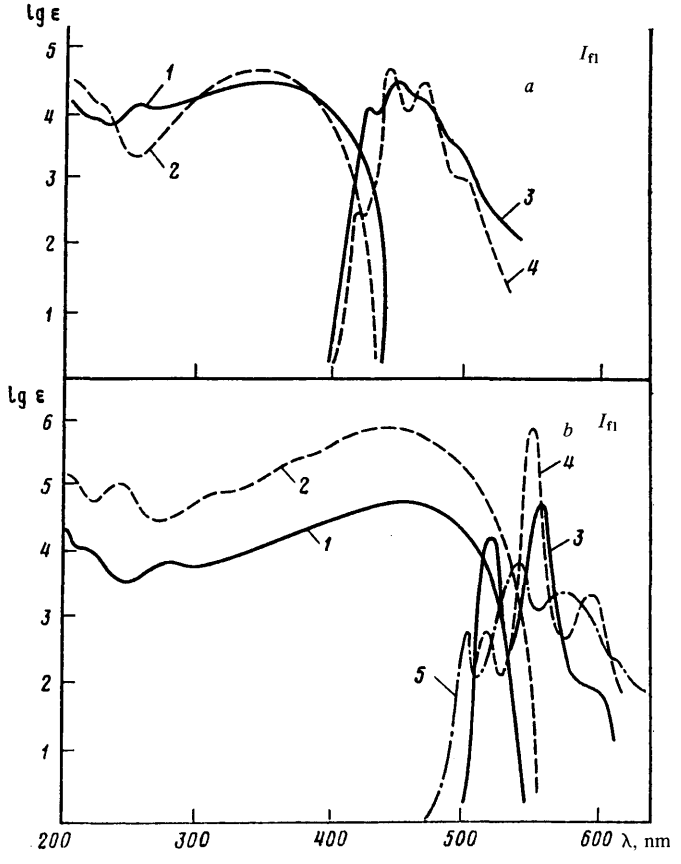
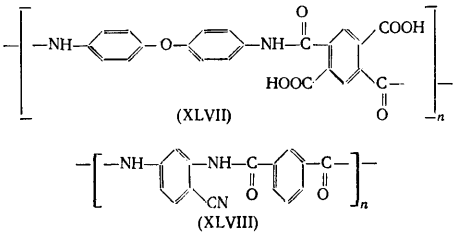


Figure 11. *a*) Absorption spectra at 20 °C (curves *1* and *2*) and fluorescence spectra at −196 °C (curves *3* and *4*) of solutions of the polymer (XLIII) (curves *1* and *3*) and the model (XLIV) (curves *2* and *4*) in concentrated H_2SO_4; *b*) absorption spectra at 20 °C (curves *1* and *2*) and fluorescence spectra at −196 °C (curves *3* and *4*) of solutions of the polymer (XLV) (curves *1* and *3*) and the model (XLVI) (curves *2* and *4*) in H_2SO_4 and the fluorescence spectrum of a powder of the polymer (XLV) at −196 °C (curve *5*).[85]

It is known[93] that the poly-Schiff bases derived from benzil and *p*-phenylenediamine have a resistivity of ~10^{12} Ω cm in the dark and an activation energy for conduction in the range 0.1–0.3 eV. In our view, one of the urgent problems, which have been only partly solved for the low-molecular-weight photoconductors,[94] is the establishment of a correlation between the fluorescence and photoconductivity of the polymer systems.

We shall consider the luminescence properties of aromatic polyamides. It is usually suggested[95] that unsubstituted polyamides of the type of poly-*m*-phenyleneisophthalamide exhibit a blue fluorescence with λ_{max} = 445 nm, caused by the presence of impurities in the polymer. When certain substituents are introduced into the aromatic rings of the polyamides, an intrinsic fluorescence appears. Thus a film of the polyamidoacid (XLVII) fluoresces with λ_{max} = 470 nm, while the polycyanamide (XLVIII) fluoresces with λ_{max} = 425 nm:[96,97]



The first studies on the optical properties of phosphor-containing aromatic polyamides and polyureas date back to the middle 1970's.[86,87,90] The polarised fluorescence of the polyamidoacid (XLIX), containing a luminescent label in the main polymer chain, has been investigated.[87] Unfortunately the authors do not quote data concerning the nature and types of binding of the phosphor fragments in the chain.[87] It is only stated that each label is enclosed between flexible hinged C–O–C junctions and that there is one label for each 300 amidoacid units. The data for solutions of the polymer (XLIX) in DMF and in DMF–glycerol mixtures revealed a linear relation between the reciprocal of the polarisation of the luminescence and T/η, where T is the temperature and η the viscosity of the solvent.

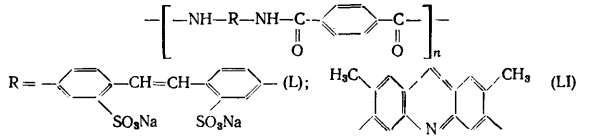
Having calculated the diffusion parameters, the authors[87] concluded that the macromolecules of the polymer (XLIX) exhibit an appreciable kinetic flexibility compared with carbochain polymers. It has been shown that the main inhibiting factor in the kinetically flexible chain of the polyamidoacid is the external viscous friction of the units against solvent molecules.

The synthesis and fluorescence properties of aromatic polyamides and polyureas with three types of phosphor fragments in the chain have been described.[86,90] The polymers were obtained by the interfacial polycondensation of Acridine Yellow, thionine, or the sodium salt of 4,4′-diaminostilbene-2,2′-disulphonic acid with acid dichlorides such as terephthaloyl chloride and sebacyl chloride or with 2,4-tolylene di-isocyanate.

Apart from the synthesis of fluorescent polymers and the comparison of their optical properties with those of the initial phosphor diamines, the authors[86] were also interested in the polyelectrolyte character of all the polyamides and polyureas investigated. The polymers synthesised do not melt up to 300 °C and are soluble in water (polymers with stilbene units in the chain) or in *NN*-dimethylacetamide and DMF (polymers with acridine and thionine units).

A detailed study of the fluorescence properties of the polymer solutions showed that the positions of the maxima in their fluorescence spectra and their fluorescence intensity depend significantly on the concentration of the solution. Thus, for the polymers with stilbene and acridine units, the maximum in the fluorescence spectrum undergoes an appreciable hypsochromic shift (by 20–40 nm depending on the type of polymer) and the concentration of the polymer in solution diminishes from 10^{-3} to 10^{-7} M (calculated in terms of the concentration of phosphor groups). The fluorescence intensity diminishes in the same sequence by a factor of 10–25 for the stilbene-containing polymers and by a factor of 150–300 for the acridine-containing polymers.

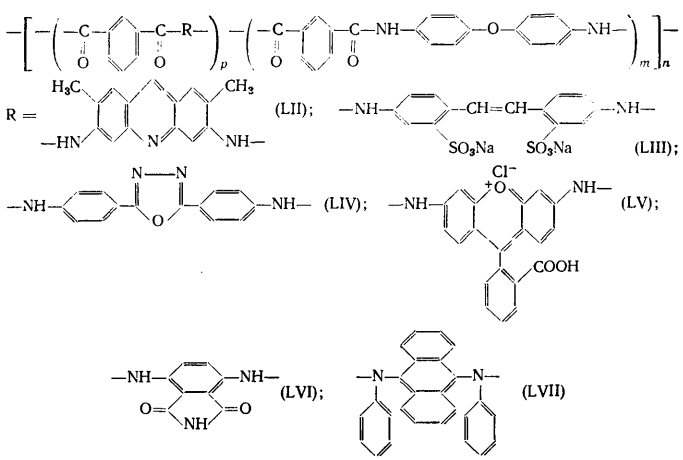
Comparison of the fluorescence characteristics of the initial phosphors and the corresponding polymers showed that the position of the maximum in the fluorescence spectra is determined by the type of polymer. For example, whereas the sodium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid luminesces with λ_{max} = 444 nm in aqueous solution at a concentration of 10^{-4} M, polyureas luminesce with λ_{max} = 440 nm at the same concentration of phosphor groups, while the emission from the dissolved polyamide based on terephthaloyl chloride (L) is at 504 nm:



The authors believe[86] that the appreciable bathochromic shift of the fluorescence band in the spectrum of the last polymer relative to the initial diamine is associated with the increased length of the conjugation chain in it. To a lesser extent, this effect is manifested in acridine-containing polymers: a band with λ_{max} = 510 nm is characteristic of the fluorescence spectra of solutions of the polyamide (LI) based on terephthaloyl chloride (compared with λ_{max} = 500 nm for solutions of Acridine Yellow).

An interesting result of the study of Uno and Kondo[86] is data showing a decreased intensity of the fluorescence of solutions of the polymers (L) and (LI) compared with the solutions of the initial phosphors under ultraviolet irradiation. It was observed that, after irradiation for 1.5 h, the intensity of the fluorescence of solutions of the sodium salt of 4,4'-diaminostilbene-2,2'-disulphonic acid falls by 56.0%, while that of solutions of the corresponding polyamide (L) falls by only 26.7%. For Acridine Yellow and the polyamide (LI), the corresponding figures are 18.4% and 6.5% respectively. The authors[86] correctly attribute the lower photoconductivity of solutions of the stilbene monomer compared with the polymer (L) to the effective *cis–trans* photoisomerisation of the former compound under irradiation conditions. The complete lack of data concerning the absorption and fluorescence spectra of the polymer specimens in the form of films is one of the disadvantages of the study by Uno and Kondo.[86]

Polyamides with a structure similar to that of the polymers described above, containing acridine [polymer (LII)], stilbene [polymer (LIII)], and diphenyloxadiazole [polymer (LIV)] units in the chain have been obtained by the present author and his co-workers:[88,89]



The proposed method of synthesis involving the polycondensation in solution of a mixture of di(aminophenyl) ether and the phosphor diamine with isophthaloyl chloride made it possible to obtain polymers with a fairly high molecular weight, in contrast to interfacial polycondensation.[86,90] Furthermore it permitted the variation of the content of the phosphor groups in the chain within broad limits by altering the ratio of the initial diamines.

The real content of the chromophoric groups in the polyamides (LII) and (LIV) was determined spectrophotometrically—from the intensities of the absorption bands with maxima at 468, 360, and 342 nm respectively.[89] It was found that the experimental concentration of the chromophoric groups is several times lower than expected on the basis of the molar ratios of the diamines used for the polycondensation. The evident cause of this discrepancy is the low reactivity of the initial phosphor diamines, as a result of which a considerable proportion of the latter fail to react.

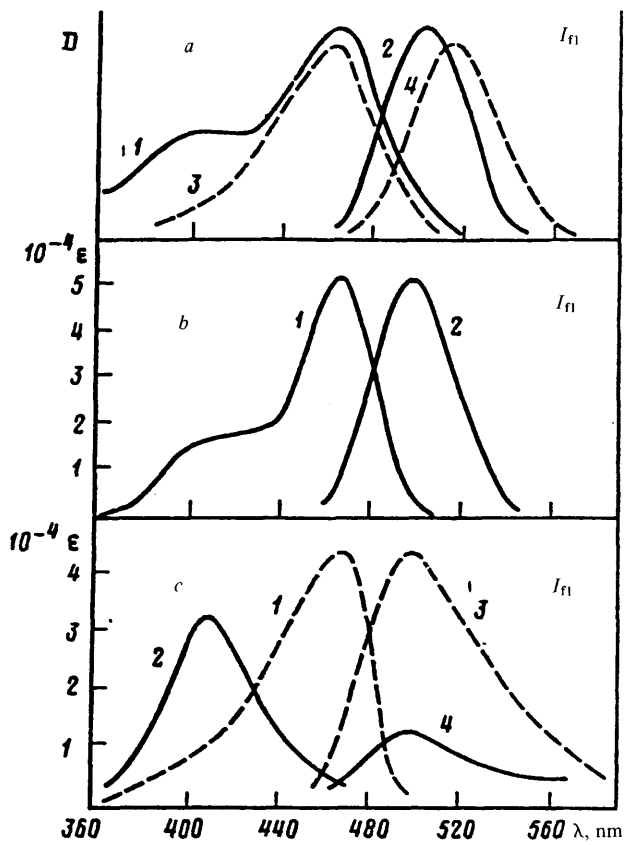
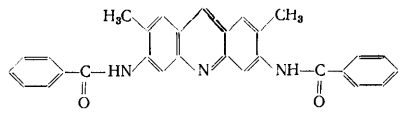


Figure 12. Absorption and fluorescence spectra of acridine-containing compounds: *a*) absorption (curves *1* and *3*) and fluorescence (curves *2* and *4*) spectra of a solution of the polyamide (LII) ($p:m$ = 1:110) in *N*-methylpyrrolidinone (curves *1* and *2*) and in the form of a film (curves *3* and *4*); *b*) absorption (curve *1*) and fluorescence (curve *2*) spectra of a solution of the polymer (LVIII) in *N*-methylpyrrolidinone; *c*) absorption (curves *1* and *2*) and fluorescence (curves *3* and *4*) spectra of solutions of Acridine Yellow in ethanol (curves *1* and *3*) and dimethylformamide (curves *2* and *4*).[89]

Fig.12*a* presents the absorption and fluorescence spectra of the polyamide (LII), with acridine units in the chain, in the form of a film and a solution in *N*-methylpyrrolidinone. The absorption and fluorescence spectra of the model diamide (LVIII) were studied simultaneously (Fig.12*b*).



(LVIII)

It follows from Fig.12 that the long-wavelength absorption and fluorescence bands of the polymer are similar to the corresponding bands of the model compound (LVIII). These data serve as an adequate basis for the assignment of the observed absorption and emission bands of the test polymer to the acridine unit.

The band with the maximum at 410 nm in the absorption spectra of solutions of the polyamide (LII) with acridine units must be attributed to the interchain association of these units. It is known[98] that acridine dyes such as Acridine Yellow tend to self-associate in solutions and the tendency is determined by the nature of the solvent. Thus it has been found that in solutions in DMF the compound is present mainly in the form of associated species characterised by an absorption maximum at 410 nm (Fig.12*b*). In the course of measurements of the absorption spectra of polyamides with different contents of Acridine Yellow fragments, it was found that a decrease in their concentration reduces the optical density ratio D_{410}/D_{465}. Spectroscopic studies of the absorption and fluorescence of solutions and films of polyamides modified by stilbene and diphenyloxadiazole units yielded analogous results.

It follows from data for the fluorescence of polyamide films that the intensity of their emission falls appreciably with increased content of the phosphor groups in the chain, which may be due to both the association of these groups and to the manifestation of the concentration-induced quenching of the fluorescence.[89]

The question of the influence of the phosphor groups in the polyamide chains on the resistance of the latter to ultraviolet irradiation is of independent interest. It is known[99] that the addition of organic phosphors increases in many instances the resistance of polymers to the action of light. After irradiation of polymer films with the unfiltered light of a DRSh-500 lamp for 2 h, it was found that the values of η_{log} for solutions of the polyamides (LII), (LIII), and (LIV) are 74, 85, and 35% respectively relative to the initial value of η_{log}.[89] After the photoageing under the same conditions of a polyamide having an analogous structure but without phosphor groups, η_{log} was found to amount to 61% of the initial value.

It is seen from the data presented that the introduction of acridine and stilbene units increases the photostability of polyamides, while the introduction of diphenyloxadiazole fragments reduces it. A possible explanation of the protective effect of the phosphor fragments may be the fact that the excitation energy of the macromolecules is transferred to these fragments, which have low-lying S_1 levels, and is emitted in the form of the $S_1 \rightarrow S_0$ fluorescence. This protective mechanism may not operate in the diphenyloxadiazole-containing polyamide, where the S_1 levels are too high.

The present author and his co-workers[88,89] synthesised also a whole series of film-forming aromatic polyamides with rhodamine [compound (LV)], 3,6-diaminophthalimide [compound (LVI)], and 9,10-dianilinoanthracene [compound (LVII)] phosphor units, present in the residue of the diamine component, or the 9,10-diphenylanthracene-*pp'*-dicarboxylic acid (LIX) units in the acid component. Most of the features found in the variation of the properties of the polyamides (LII) and (LIII), for example, the increase of η_{log} with decreased content of the phosphor fragments in the chain or the weakening of the fluorescence intensity of the films with increased concentration of these fragments, are also observed with the polyamides (LIV)–(LVII) and (LIX).

As an example, Fig.13 presents the absorption and fluorescence spectra of solutions and films of the polyamides (LVII) and (LIX) and also solutions of the corresponding monomers—9,10-dianilinoanthracene and 9,10-diphenylanthracene-*pp'*-dicarboxylic acid. It follows from the results of the study of the luminescence-spectroscopic properties of these compounds and also the polyamides (LV) and (LVI) and the corresponding monomers that the chromophoric fragments are responsible for the fluorescence and long-wavelength absorption of the polymers (LV)–(LVII) and (LIX).

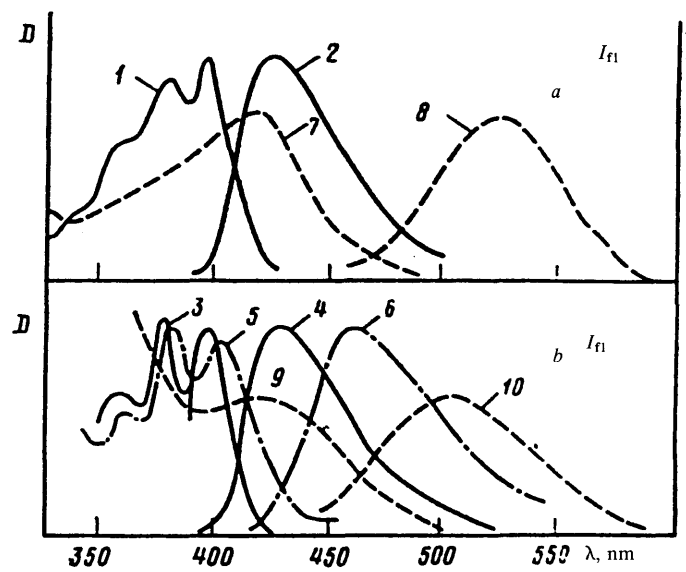


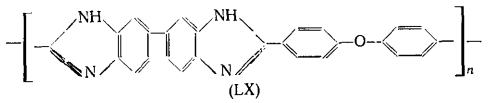
Figure 13. *a*) Absorption (curves *1* and *7*) and emission (curves *2* and *8*) spectra of solutions of 9,10-diphenylanthracene-*pp'*-dicarboxylic acid (curves *1* and *2*) and 9,10-dianilinoanthracene (curves *7* and *8*) in dimethylacetamide; *b*) absorption (curves *3*, *5*, and *9*) and emission (curves *4*, *6*, and *10*) spectra of a film of the polyamide (LIX) (curves *5* and *6*) and solutions in dimethylacetamide of the polyamides (LIX) (curves *3* and *4*) and (LVII) (curves *9* and *10*); for the polyamide (LVII), $p:m = 1:10$.[88]

Certain representatives of the polyamides (LII)–(LIX), capable of forming transparent intensely fluorescent films, are promising as scintillating materials suitable for recording of the tracks of α- and β-particles and neutrons and for X-ray dosimetry.[4]

3. Polyheteroarylenes

Aromatic polymers with a heterocyclic fragment in the chain, which possess very effective mechanical and dielectric properties and a high thermal stability, belong to the class of polymers which have been least investigated from the standpoint of their light absorption and fluorescence properties. There have been only a few studies of the spectroscopic properties of polybenzimidazoles,[100] polybenzoxazoles,[101,102] polyimides,[96,103,104] polyhexazocyclanes,[105] and polymeric bipyridylium salts.[106]

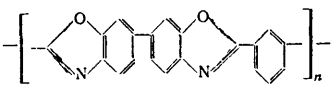
It has been stated in a report[100] that solutions of the polybenzimidazole (LX) in *NN*-dimethylacetamide and formic acid fluoresce in the blue part of the spectrum.



(LX)

The spectroscopic properties of the polymer (LX) were compared with those of the model bis-*p*-(2-benzimidazolyl)-phenyl ether (Fig.14). It was found that the fluorescence of the model is determined by the radiative transitions from the 0–0, 0–1, and 0–2 vibrational levels of the excited ^1L_b state of the benzimidazole ring, while the fluorescence spectrum of the polymer (LX) has a vibrational structure; λ_{max} = 394 and 413 nm. In addition to the monomer luminescence band, the emission spectra of solutions of the polymer (LX) and of the model compound in formic acid contain a longer-wavelength band at 460 nm associated with the fluorescence of the intermolecular associated species, which undergoes a bathochromic shift with increase in the concentration of the solution.

The available information in the literature about the fluorescence properties of polybenzoxazoles is even more scanty. Thus an intense green fluorescence of films of the polymer (LXI) with λ_{max} = 490 and 520 nm has been mentioned;[101,102] the authors confined themselves to the measurement of the emission spectrum without attempting to account for its origin.



(LXI)

The possibility of the fluorescence of aromatic polyimides of different structure has been discussed by the present author and his co-workers.[96,103,104] They showed that, regardless of the presence of phosphor fragments in the chain, the quenching of the fluorescence associated with the nature of the diimide unit is observed in polypyromellitimides. In the study of the spectroscopic characteristics of the model compound *NN'*-dimethylpyromellitimide (LXII) it was observed[96] that this product does not fluoresce at room temperature (in solution) and exhibits an intense phosphorescence at −196°. The absorption and phosphorescence spectroscopic data suggested a scheme for the arrangement of the energy levels in the molecule of (LXII), the characteristic details of which are a low-lying $T_{\pi\pi^*}$ level (20000 cm^{-1}) and the fact that the energy of the $S_{n\pi^*}$ state is intermediate between those of the $S_{\pi\pi^*}$ and $T_{\pi\pi^*}$ states. It is known[69] that molecules with this arrangement of levels do not fluoresce. The quenching of their fluorescence is associated with the probability of a radiationless intersystem crossing from the $S_{n\pi^*}$ level to the $T_{\pi\pi^*}$ level.

The energies of the $S_{n\pi^*}$ and $T_{n\pi^*}$ levels of compound (LXII) can increase on protonation of the pyromellitimide ring. Indeed, it has been shown[96] that in solution in concentrated sulphuric acid the intersystem crossing process becomes unlikely as a consequence of the increase in the energy of the $S_{n\pi^*}$ state, which has been confirmed by the appearance of an intense green fluorescence of compound (LXII) under these conditions.

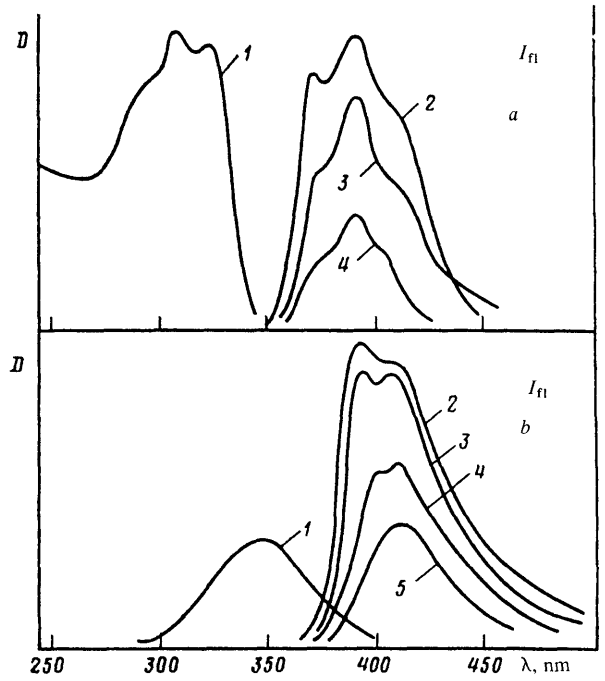
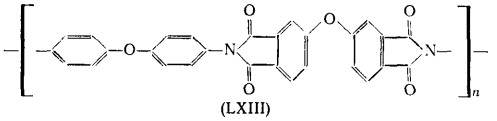


Figure 14. a) Absorption (curve *1*) and fluorescence (curves *2–4*) spectra of solutions of bis-*p*-(2-benzimidazolyl)-phenyl ether in dimethylacetamide at concentrations of 7.9 × 10^{-4} g ml^{-1} (curve *2*), 3.2 × 10^{-3} g ml^{-1} (curve *3*), and 6.3 × 10^{-3} g ml^{-1} (curve *4*); b) absorption (curve *1*) and fluorescence (curves *2–5*) spectra of solutions of the polymer (LX) in dimethylacetamide at concentrations of 4.6 × 10^{-6} g ml^{-1} (curve *2*), 1.5 × 10^{-4} g ml^{-1} (curve *3*), 4.3 × 10^{-4} g ml^{-1} (curve *4*), and 5.2 × 10^{-3} g ml^{-1} (curve *5*).[100]

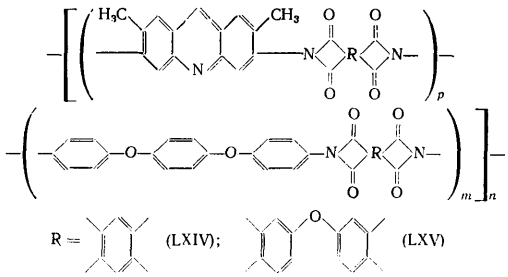
Thus the quenching of the fluorescence in polypyromellitimides is due to the presence of low-lying $n\pi^*$ levels. The appearance of fluorescence in aromatic polyimides requires that a diimide component with higher $S_{n\pi^*}$ and $T_{n\pi^*}$ levels be introduced into their composition. For example, the polyimides based on the dianhydride of oxydi(benzene-3,4-dicarboxylic acid) such as the polymer (LXIII) exhibit an appreciable blue fluorescence:[103]



(LXIII)

A comparative study of the spectroscopic properties of the polypyromellitimides (LXIV) and the polyimides (LXV) with acridine fragments in the chain has been carried out.[104]

The polymers were synthesised by the low-temperature polycondensation of a mixture of Acridine Yellow and the di(4-aminophenyl) ether of hydroquinone with the dianhydrides of the corresponding tetracarboxylic acids with subsequent thermal polycyclodehydration of the prepolymer films:



R = (LXIV); (LXV)

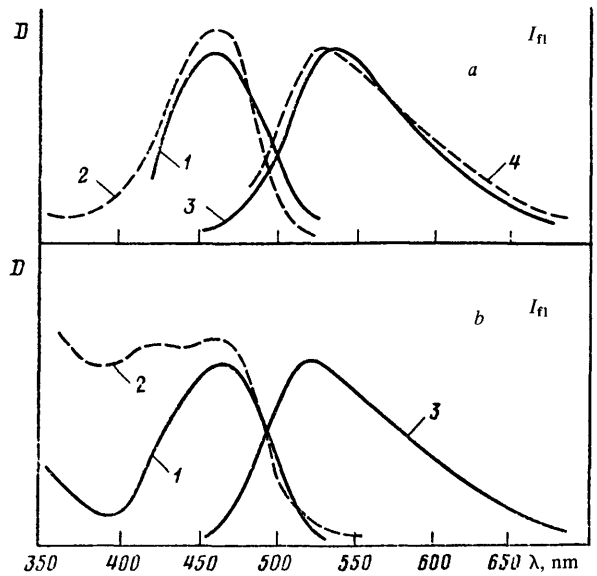
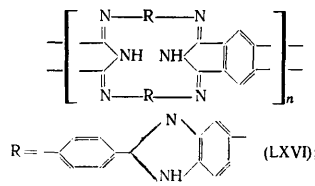


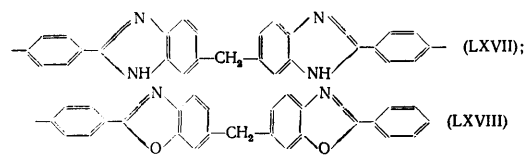
Figure 15. *a*) Absorption (curves *1* and *2*) and emission (curves *3* and *4*) spectra of films of the prepolymer for the polyimide (LXV) (curves *1* and *3*) and the prepolymer for the polyimide (LXIV) (curves *2* and *4*); *b*) absorption (curves *1* and *2*) and emission (curve *3*) spectra of films of the polyimides (LXV) (curves *1* and *3*) and (LXIV) (curve *2*); in all cases $p:m = 1:3$.[104]

Acridine-containing polyamidoacids showed an intense green fluorescence with λ_{max} = 500 nm in solutions and a yellow-green fluorescence with λ_{max} = 530–540 nm in films (Fig.15*a*). Fig.15, which presents the absorption and emission spectra of films of the polyimides (LXIV) and (LXV) as well as the corresponding polyamidoacids, shows that the nature of the dianhydride component has little influence on the spectroscopic properties of the prepolymers. On the other hand, the luminescence-spectroscopic characteristics of the polyimides depend strongly on the character of the diimide fragment (Fig.15*b*). Whereas the absorption spectra of the polyimide (LXV) contain only one band with λ_{max} = 460 nm, in the spectra of the polyimide (LXIV) an absorption band with a maximum at 415 nm, associated with the aggregation of the acridine fragments, appears. Regardless of the ratio $p:m$, all the polyimides (LXV) showed an intense fluorescence with λ_{max} = 515–525 nm, whereas the polyimides (LXIV) did not fluoresce.[104]

The aim of the synthesis of the acridine-containing polyimide (LXV) as well as other polyheteroarylenes–polyhexazocyclanes (LXVI)–(LXVIII), described by the present author and his co-workers,[105] was the preparation of polymeric phosphors with yellow and orange luminescence, which are of interest for the preparation of scintillating materials:[108]



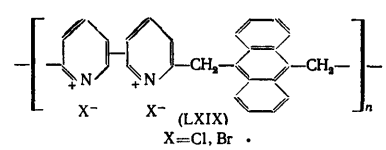
R = (LXVI);



(LXVII); (LXVIII)

The polymers (LXVI)–(LXVIII) were synthesised by the polycondensation of pyromellitonitrile with diamines of the phenylbenzimidazole and phenylbenzoxazole series in phenol. It was found that the absorption and fluorescence spectra of these polymers as well as the model hexazocyclanes of analogous structure contain bands in the ultraviolet region associated with the electronic transitions in the phenylbenzimidazole and phenylbenzoxazole fragments; in addition, the fluorescence spectra contain longer-wavelength bands at 540–650 nm associated with charge transfer from the electron-donating chromophoric fragment to the electron-accepting isoindole fragment.

In conclusion we shall consider the absorption and fluorescence properties of polymeric bipyridylium salts (polyviologens) (LXIX), obtained[106] by the Menshutkin reaction of 2,2'- or 4,4'-bipyridyl with 9,10-dihalogenmethylanthracenes in methanol, DMF, or dimethyl sulphoxide at 30–70 °C. The solubility in water and intense fluorescence of these polymers make it possible to use them as luminescent probes for the investigation of biological membranes:[63]



(LXIX)
X=Cl, Br .

The absorption and emission spectra of solutions of the polymers (LXIX) as well as the model (9-methyl)-10-anthrylmethylpyridinium halides (LXX) and the initial 9,10-dihalogenomethylanthracenes (Fig.16) have been investigated. It was found that the absorption spectra of the corresponding chloro- and bromo-compounds have a resolved structure typical for anthracene derivatives; the absorption spectra are fairly close to one another as regards the shape of the bands and their relative positions. On the other hand, appreciable differences were noted in the fluorescence

properties of the monomers, the model compound (LXX), and the polymers (LXIX). Thus, whereas 9,10-dichloromethylanthracene and the corresponding model compound exhibit a weak fluorescence in the crystalline form and in solution, the polyviologens show a bright fluorescence both in the solid state and in solution. Furthermore, 9,10-dibromomethylanthracene and the corresponding model compound do not fluoresce at all either in the solid state or in solution at room temperature, while the bromine-containing polyviologen (LXIX, X = Br) exhibits an intense fluorescence under these conditions.

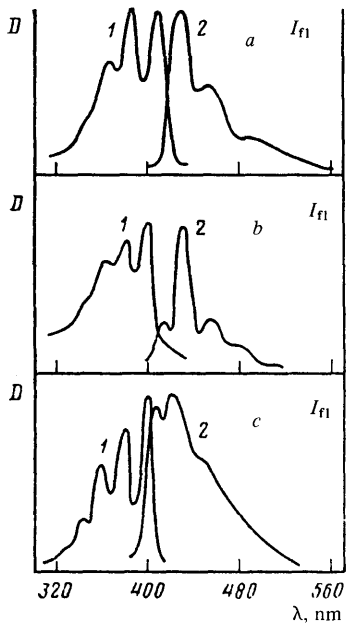


Figure 16. Absorption (curve *1*) and fluorescence (curve *2*) spectra of solutions in dimethylformamide: *a*) of 9,10-dichloromethylanthracene; *b*) of the model compound (LXX, X = Cl); *c*) the polyviologen (LXIX, X = Cl).[106]

The present author and his co-workers[106] suggested as an explanation of the observed differences that in dichloromethylanthracene and especially in dibromomethylanthracene the probability of the radiationless transitions from the S_1 to the T_1 level increases as a consequence of the strong spin–orbital interaction and such transitions are responsible for the quenching of the fluorescence. Halide ions have been detected in polymers in the vicinity of the nitrogen atoms of the bipyridyl residues, which tends to increase the number of vibrational degrees of freedom, reduces the probability of radiationless transitions, and thereby increases the fluorescence quantum yield. The differences between the emission spectra of the polymers (LXIX) and the corresponding model compounds (LXX) are apparently associated with the fact that the bipyridylium salts,[107] which do not contain anthracene fragments, have fluorescence spectra with a set of intense bands in the range 400–450 nm, in contrast to pyridinium salts.

Thus the examples examined above show that, among heterocyclic aromatic polymers, the luminescence-spectroscopic properties have been more or less investigated only for polyimides. The properties of other polyheteroarylenes have been either very little investigated (polybenzimidazoles, polybenzoxazoles, and polyhexazocyclanes) or not at all (polyoxadiazoles, polyquinoxalines, polyquinazolinones, and a whole series of other polymers). At the same time the study of the fluorescence characteristics of these polymers is of undoubted interest, since it is known[4] that many of their low-molecular-weight analogues exhibit an intense fluorescence.

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Summarising the available information about the fluorescence characteristics of condensation polymers, one may conclude that the introduction of phosphor fragments into the composition of the macromolecules can lead to the preparation of materials with an intense luminescence and in many cases with a high photostability and photosensitivity. The specific synthesis of such polymers, which have a high fluorescence quantum yield in the required spectral range, makes it possible to create promising materials for the needs of scintillation and laser technology, for the preparation of migration-resistant luminescent varnishes and dyes, and for medical and biological research. The study of the behaviour of polymers with fluorescent labels in the chain by optical molecular spectroscopic methods enables us to obtain new information, which is either totally unobtainable or obtainable with difficulty by other procedures, about the dynamic mobility of macromolecules in the solution, about the conformational structure of polymers, etc.

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