INVESTIGATION OF INTERMOLECULAR INTERACTIONS IN SOLUTION POLYMER - ORGANIC DYE BY METHOD ELECTRONIC SPECTROSCOPY

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SUMMARY: It has been shown that specific electrostatic interactions between charges of ion dyes and functional groups of polymer play main role in the cause of polar coulored matrices. These interaction prevent by formation tight ion pairs of dyes and their associates. Therefore, such matrices have practically the same electronic spectra as liquid solution of dyes. Electrostatic interactions between dye counterions dominate in low polarity polymer matrices. Process of formation tight ions pair is became easier. Such pairs cause quenching of the fluorescence and distortion of electronic spectra by comparison with liquids.

Introduction

Coloured polymeric matrices have a number of operational advantages compared with liquid media 1). However these advantages can be realised only if the spectral, luminescence, properties of dyes do not significantly change with the adoption of polymer matrices, compared with the solution of these dyes in liquids 2).

Among other organic dyes, polymethine (cyanine) dyes exhibit the most versatile absorption and luminescence characteristics 2). Note that, even on going from one class of dyes to another, change in these properties is not always so significant as in molecular engineering of cyanine structure. For this reason, polymethine dyes are being used for resolving diametrically opposite task objectives related to conversion of radiant energy 1). No doubt that any new approaches to controlling the spectral, luminescence properties of coloured matrices based on cyanines are of current interest from both the academic and practical points of view.

Results and discussion

The introduce of salt-like symmetrical and unsymmetrical polymethine dyes into polystyrene and polymethylmethacrylate led to a marked distortion of their spectral, luminescence properties. Compared with the solution of polymethines in 1,2-dichloroethane, a new band

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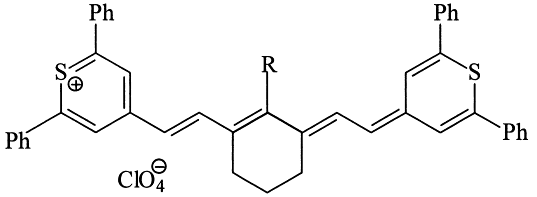
appears at the short-wavelength edge of the absorption spectrum of many of these dyes and the intensity of the long-wave band decrease. An example of such behaviour is that exhibited by thiopyrilotricarbocyanine **1** (Fig.1) These changes are accompanied by the quenching of



1, R=H; **2**, R=Ph

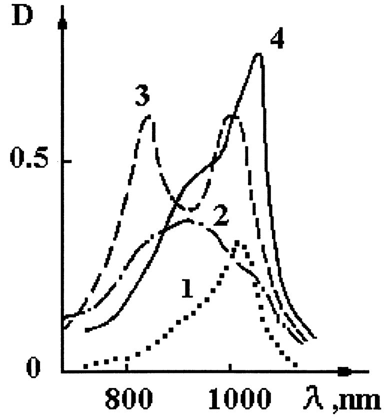


Fig. 1: Absorption spectra of a solutions of dye **1** in 1,2-dichloroethane (1) and films of polystyrene (2), polymethylmethacrylate (3) and polyurethane (4). Dye concentrations 10^{-4} mol litre^{-1} (1) and 5x10^{-7} mol g^{-1} (2-4). Film thickness 69 μm (1) and 70 μm (2-4). D – is optical density.

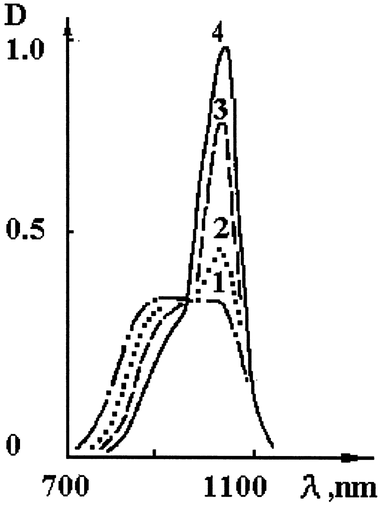


Fig. 2: Absorption spectra of a films of dye **2** in polystyrene (1), copolymer methylmethacrylaate and styrene in ratio 1:4 (2), 4:1 (3) and polymethylmethacrylate (4). Dye concentration – 10^{-6} mol g^{-1} of polymer. Film thickness 60 μm.

fluorescence. It has been shown that the described effects are caused by the formation of tight ion pairs and their associates. These associates have “sandwich” structure. Unsymmetrical polymethine dyes form tight ion pairs rather than symmetrical dyes. It is caused by greater nonuniform charge distribution in cations unsymmetrical dyes.

Cyanines in weakly polar media readily associate at much lower concentrations (10^{-5} – 10^{-6} mol litre^{-1}) than in strongly polar media (10^{-2} – 10^{-3} mol litre^{-1}) 3). Therefore, it is difficult to prevent the formation of associates by the variation of the concentration of polymethine dyes in polymer films. The necessary optical density of such films can be ensured only if the concentration of the dye is several orders of magnitude higher than the concentration used in the determination of the absorption spectra in a cell 1 cm thick.

As in the case of liquid solvents, a change in their matrix polarity affects the spectral, luminescence, and nonlinear properties of polymethine dyes 4). An investigation of the electronic spectra of thiopyrilotricarbocyanine **2** in copolymer films with different rations of the components (styrene and methylmethacrylate) has shown (Fig. 2) that an increase in the content of the less polar and nucleophilic component (styrene) in the copolymer increases the intensity of the short-wavelength band and induces its hypsochromic shift. This quenches the original luminescence band. The existence of an isobestic point, the dependence of the spectra on the nature of the anion, and the failure of the dye **2** solutions in copolymer to obey the Lambert-Beer law all support the existence of an equilibrium between ion pairs and their associates. In pure polystyrene the equilibrium shifts almost completely towards associates (Fig. 2). Consequently, even thiopyrilotricarbocyanine **2** with bulky meso-substituent in the matrices characterised by a very low polarity and a weak nucleophilicity may preferentially assume the associated state in which a major change occurs in the spectral, luminescence compared with the corresponding properties of liquid solutions.

It follows from this account that the tendency of salt-like polymethine dyes to form ion pairs and their associates can be reduced by the use of high-permittivity (ε) polymers. However, the development of such polymers is very problematic. The most widely used polymers are characterised by $\varepsilon < 10$ 5), so that dyes in the polymers are not fully dissociated. It has been proposed that the dissociation of salt-like cyanines in low-ε matrices can be facilitated by embedding cation polymethine dyes in polymers containing strongly nucleophilic groups. These groups solvate positively charged centers of a cation , move apart counterions, and to a lesser degree prevent the formation of closely spaced ion pairs. A similar effect can be achived in anion dyes embedded in polymer with electrophilic groups by the electrostatic interactions of these groups with negative anion charges. Solvated ion pairs have practically the same electron spectra as solvated ions 6) and, therfore, the formation of such pairs in a polymer should not significantly alter the spectral and luminescence properties of polymethine dyes compared with their solutions in liquids, even if the cyanines are fully dissociated in such liquids.

Spesific solvation of polymethine dye ions by nucleophilic (electrophilic) groups in a polymer also weakens the electrostatic and dispersive interactions between the chromophores of these ions, which additionally hinders the association of the ions. Strongly nucleophilic properties are exhibited by cellulose diacetate, polyvinyl butyral, epoxides, polyimides, and polyurethane. These polymers also have a higher permittivity than polymethylmethacrylate 5). Consequently, even thiopyrilotricarbocyanine 1 with a very strong tendency to association and unsubstituted at the meso position, do not aggregate and retain the same form as in liquid solvents (Fig. 1).

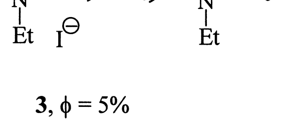
Coloured materials based on polyurethane are particularly promising, because this matrix not only contain strongly nucleophilic groups (the nucleophilicity of the polyurethane are comparable with that of dimethylformamide) but also has one of the highest value of ε among polymers. It has been used in the development of coloured materials for laser technology that have good operational characteristics 7-9).

Because of low fluorescence quantum yields ϕ 1, 2), the most of polymethine dyes cannot be regarded as typical luminophors. For cyanines with an open polymethine chain, the values of ϕ are far from 100 % even in case of optimal end heterocycles 1, 2).

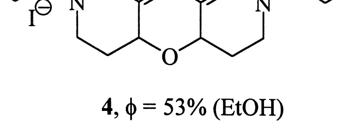
This can be explained by the fact that the main pathway for nonradiative deactivation of electronically excited states is the trans-cis-photoisomerization caused by rotation around the chain bonds in the excited state 2). Rotation in the excited state is favored by a decrease in the bond order upon excitation 2). Therefore, the quantum yield of cyanines fluorescence can be enhanced by suppressing the formation of photoisomers.

This can be achieved by crosslinking the elements of the polymethine chain with saturated bridging groups.

The value of ϕ markedly increases upon complete cyclization of the chain in trimethinecyanines, as is illustrated by the dyes **3** and **4**:



3, $\phi = 5\%$

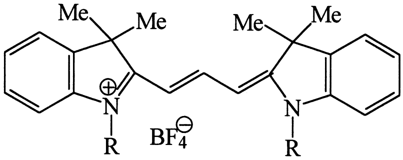


4, $\phi = 53\%$ (EtOH)

The attempts to rigidize the polymethine chain in pentamethinecyanines and higher vinylogs have been unsuccessful so far. Partial cyclization of chromophore (covering even a significant number of chain bonds) was found to be insufficient [2)].

Another way to suppress photoisomerization is the use of polymer matrices, in which dyes do not form associates. In this case, we can rigidize cyanines with any length of the polymethine chain.

Proper selection of polymers and dyes can provide a stronger increase in ϕ for mono- and carbocyanines than complete cyclization of the polymethine chain. For example, upon embedding in polyurethane, ϕ attains values of **72%** for thiacarbosyanine **3** and 93% for astraphloxine **5.**



5, R = Me; **6**, R = CH_2CH_2OH

Marked increase in ϕ for cyanines in polymer matrices is attained because the structure of dye molecules is rigidized virtually without changes in their molecular structure. Moreover, polymer matrices suppress not only photoisomerization but also luminescence quenching upon diffusion-controlled collisions with oxygen and other quenching impurities.

Another important advantage of polymer matrices is that Stokes' shift has more the value in polymer than by crosslinking of the polymethine chaine. For example, on going from thiacarbocyanine **3** to its rigidized analog **4**, the Stokes' shift (in ethanol) decreases by 140 cm^{-1} while, upon embedding **3** in polyurethane, it even increases by 25 cm^{-1} (compared to ethanol solution). Unsymmetrical polymethine dyes also conserves high Stokes' shift in polymers.

Therefore, polymer matrices can provide some rigidity sufficient for attaining maximum quantum yields of polymethines fluorescence. At the same time, the structural mobility of the excited molecules remains fairly sufficient for realization of the four-level scheme of electronic transitions which ensures high Stokes' shifts.

The observed ability of polymethine dyes to markedly increase their fluorescence quantum yields on going from liquid solutions to polymer matrices, on retention of high Stokes' shifts, allowed us to suggest a new, unconventional field of application for cyanines, namely, as luminescent concentrators of solar energy [1,2]. Being embedded into a polymer matrix, even not best polymethines were found to provide higher coefficient of energy concentration than the widely spread luminophor Rhodamine 6G. Under similar conditions, this coefficient was found to be 3.1 and 2.4 for dye **3** and Rhodamine 6G, respectively.

It was discovered that polymethine dyes wich form covalent bond with polymer matrix possess more high photostability, radiation damage threshold and fluorescence quantum yields than analogous cyanines are indroduced in polymer as mechanical impurity. Such picture is observed for dye **6** in comparison with dye **5** in polyurethane. The first cyanine is sewed on polymer matrix due to interaction its hydroxyl groups with isocyanate groups of polyurethane. The chemical sewing enhances rigidity of structure and provides output a heat from area of absorption dyes. Besides the sewing make difficult drawing near molecules dyes and consequently prevent their association.

Conclusion

Specific electrostatic interactions between charged centers of dyes and polar groups of polymers take place in solution polymer-dye. These interactions prevent by the formation of tight ion pairs and their associates. Therefore, electronic spectra of coloured matrices based on polymer containing polar groups practically coincide with spectra in liquid solvents. Besides its possess much more the value fluorescence quantum yield than coloured liquid media. Polyurethanes, epoxides, polyimides can carry out role such polymers for polymethine dyes.

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