Mendeleev Commun., 2006, **16(6)**, 300–301

Polymer films with an amphiphilic crown-ether styryl dye as a prototype of chemosensing materials

Sergei Yu. Zaitsev,*[a,b] Elena A. Varlamova,[a] Marina S. Tsarkova,[a] Irina N. Staroverova,[a] Kirill A. Gogasov,[b] Sergei P. Gromov,[c] Mikhail V. Alfimov,[c] Andrei A. Turshatov[d] and Dietmar Möbius[d]

[a] *Department of Organic and Biological Chemistry, K. I. Skryabin Moscow State Academy of Veterinary Medicine and Biotechnology, 109472 Moscow, Russian Federation. Fax: +7 495 377 4939; e-mail: szaitsev@mail.ru*

[b] *M. M. Shemyakin–Yu. A. Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences, 117997 Moscow, Russian Federation*

[c] *Photochemistry Center, Russian Academy of Sciences, 119421 Moscow, Russian Federation*

[d] *Max Planck Institute for Biophysical Chemistry, D-37071 Göttingen, Germany*

DOI: 10.1070/MC2006v016n06ABEH002398

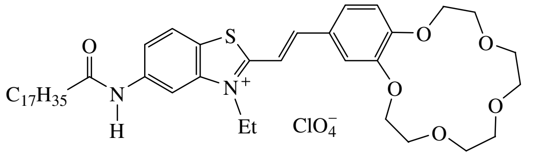
A combination of the photosensitive and ion-selective properties of thin polymer films with immobilised amphiphilic crown-ether styryl dye (in particular dye interaction with alkaline earth metal ions) gives evidence that such films can serve as a prototype of chemosensors with optical signal detection.

The synthesis and structure-functional study of the multifunctional polymeric composites are of growing interest for scientists working with supramolecular systems and nanoscale materials.[1–3] Special attention is devoted to the composites with ion-selective, photosensitive and self-assembly properties, such as amphiphilic crown ether dyes.[4–7] Our recent studies[8–10] on the monolayers and LB films of amphiphilic crown-ether dyes with variable size of the polyether ring and substitutions in the chromophoric part demonstrated the possibility of preparing photosensitive monolayer films with the ability to selectively bind particular alkali and heavy metal ions. A further important step towards the application of these systems is the preparation of polymeric thin films (thickness of 10–50 μm) with immobilised crown-ether dyes. These systems are promising sensitive components for ion detection in optical and electrochemical devices; photocontrolled extraction of metal ions; and materials for recording, storing and processing of optical information.[1–3]

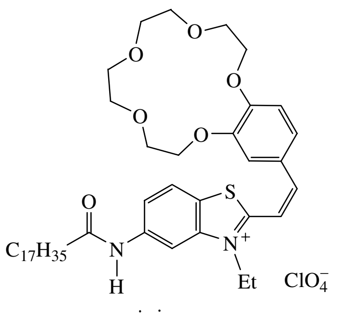
The aim of this work was to prepare and characterise polymer thin films with an immobilised amphiphilic crown-ether styryl dye, in particular, to investigate its ion-selective and photosensitive properties.

The amphiphilic benzo-15-crown-5 styryl dye (E12) was synthesised as described earlier.[9] The dye was characterised by elemental analysis, NMR and IR spectroscopy.[9]

Polystyrene (PSt) high purity standard with M_n 200000 was purchased from Aldrich. Polyvinylcaprolactam (PVC) with M_n 300000 and a copolymer (PVCSt) with M_n 900000 (PVC:PSt ratio of 10:1) were prepared and purified as described earlier.[2] The salts $KClO_4$ (99%), $Ca(ClO_4)_2$ (98%) and $Mg(ClO_4)_2$ (98%) were purchased from Merck. Water was purified with a Milli-Q filtration unit from Millipore Corp.



trans-isomer



cis-isomer

The polymer films with and without the dye (total thickness of 40±5 μm) were prepared by classical spreading techniques on the medical glass substrate (5.0×1.5 cm^2) from 10% polymer solutions in chloroform. The concentration of the dye in chloroform was 1 mM, whereas in the obtained films the average dye amount was 1.09±0.05 μg cm^{-2}. Numerous experiments showed that this dye did not dissolve in the aqueous solutions and was not extracted from the polymer films by interaction with studied salts.

The spectra of the polymer-dye films were recorded in the range 300–600 nm using a DU-90 spectrophotometer (Beckman, USA) under the following conditions: (i) 24 h dark relaxation; (ii) intense 10 min illumination at a 15 cm distance. The absorbance of the polymer films without dye was below 300 nm (maximum was about 255 nm). The experimental errors were ±1 nm for λ measurements and ±0.001 units for absorbance intensity measurements. The average data of three to four measured samples in each case are presented in Tables 1 and 2.

The influence of various cations on these films was studied using 1.0 mM $KClO_4$, $Ca(ClO_4)_2$ or $Mg(ClO_4)_2$ aqueous solutions. Each film was stored in the salt solution for 60 min, washed with distilled water and placed in distilled water for 20 min. This procedure allowed the cation interaction with the dye in the film, as well as the removal of the excess of the salt from the film afterwards (especially in the case of PVCSt). After such a washing procedure, the film was dried at 40 °C during 30 min and stored in the dark. The procedure was the same for all the films at various salt concentrations (from 3 to 9 mM).

The most important information on the dye photosensitive properties, as well as on dye–cation complexation, was gained by measuring the absorption spectra of obtained dye–polymer films under various conditions. The spectra of the dye–polymer films in all cases showed a strong band with an absorption maximum at 400–450 nm, which was assigned to the dye *trans* form according to published data[8–10] on the pure dye in some organic solvents. The pronounced shoulder at 320–350 nm was assigned to the dye *cis* form according to our preliminary studies.[9] From the original spectra, it was possible to obtain directly only the parameters of the dye *trans* form, even if its maximum was shifted. In order to obtain the parameters of the dye *cis* form, the original spectra were recalculated.[2] This allows us to estimate a relative amount of the dye *trans* and *cis* forms in the freshly prepared polymer films under various conditions (Table 1). Note that, for all polymer and copolymer films after dark relaxation, the *cis–trans* ratios of the dye (from 31.6 to 36.7%) were significantly higher than those of the dye in a chloroform solution (24.1%) due to the particular polymeric environment.

The *cis–trans* ratios of the dye in the studied films increased significantly after intense 10 min illumination, as compared to the initial values or values after dark relaxation of these films (Table 1). Such effects clearly indicate the reversible photo-

Table 1 Intensities of absorption maxima for two dye forms (*trans* and *cis*, or their ratios) in various polymer matrices.

Polymer matrix	Experimental conditions	Intensity, *trans* form	Intensity, *cis* form	*cis–trans* ratio (%)
PSt	Dark relaxation	0.049±0.001	0.018±0.001	36.7
	Illumination	0.045±0.001	0.020±0.001	44.4
PVC	Dark relaxation	0.269±0.003	0.085±0.001	31.6
	Illumination	0.189±0.002	0.087±0.001	42.0
PVCSt	Dark relaxation	0.238±0.003	0.080±0.001	33.6
	Illumination	0.180±0.002	0.085±0.001	47.2

induced conformational changes of the dye molecules depending on the polymeric environment and possibility for obtaining a particular equilibrium state between *cis* and *trans* forms. The influence of the polymeric matrix on the photoinduced conformational changes of the dye molecules can be estimated using the row PSt > PVCSt > PVC (from high to low *cis–trans* ratio values of the dye-polymer films, obtained after dark relaxation, Table 1). After intense 10 min illumination, the *cis–trans* ratios of the dye in the same films decreased in order PVCSt > > PSt > PVC (Table 1). These data can be explained by differences in the mobility of dye molecules immobilised in the polymer films. One of the main reasons for increasing dye molecule mobility in the above case (relatively high *cis–trans* ratio values for PVCSt) is the relatively low-density packing of copolymer chain, as compared to the homopolymers.[2]

Thus, the comparison of the relative changes of the *cis–trans* ratios at illumination, but not the absolute values, are the most important for the material characterization.

The ion-sensitivity of the dye-polymer films in connection with the dye photosensitivity was studied for the first time. The data for PVCSt-dye films only are shown in Table 2.

As can be seen in Table 2, in all cases, the presence of alkali or alkali-earth metal ions in aqueous solutions leads to the shift of the film adsorption maximum to the shorter wavelength. The highest shift is observed for the *trans* form ($\lambda_{1\,\mathrm{max}}$), as compared to the *cis* form ($\lambda_{2\,\mathrm{max}}$) values due to the stronger interaction of the cations with *trans* form, as compared to the *cis* form of the dye.[5] The dye interaction with alkaline earth metal ions leads to the highest shift of the film adsorption maximum (due to the complex formation of the dye with Mg^{2+} or Ca^{2+}), as compared to the values for such a typical alkali metal ion as K^+ (non-specific interaction).[4–6] This shift is almost independent of the polymer composition. The dependence of the absorption maximum shift *vs*. Mg^{2+} or Ca^{2+} concentration is almost linear. The three to four times higher shift of $\lambda_{1\,\mathrm{max}}$ for the dye-polymer film by interaction with Mg^{2+} or Ca^{2+}, as compared to K^+, can be explained by differences in the complex formation as was discussed recently[2] for similar dyes in monolayer films. It is important that only a negligible response occurs for all these systems in the presence of Hg^{2+} (chosen as a typical heavy metal ion). All these observations prove that such films can serve as a prototype of a chemosensor for alkaline earth metal ions with optical signal detection.

Table 2 Intensities of the absorption maxima for two dye forms (*trans* and *cis*, or their ratios) in the poly(vinylcaprolactam-co-styrene) films by incubation with salt solutions.

Salt	Salt concentration/ mol dm^{-3}	*cis–trans* ratio (%)	$\lambda_{1\,\mathrm{max}}$/ nm	$\lambda_{2\,\mathrm{max}}$/ nm	$\lambda_{1\,\mathrm{shift}}$/ nm	$\lambda_{2\,\mathrm{shift}}$/ nm
$KClO_4$	—	36.6	442±2	339±2	—	—
	0.001	38.8	438±2	337±2	4±2	2±2
	0.003	39.3	436±2	336±2	6±2	3±2
	0.006	41.0	435±2	337±2	7±2	2±2
	0.009	43.1	435±2	336±2	7±2	3±2
$Ca(ClO_4)_2$	—	33.5	441±2	337±2	—	—
	0.001	44.7	428±2	333±2	13±2	4±2
	0.003	47.5	422±2	334±2	19±2	3±2
	0.006	50.3	417±2	330±2	24±2	7±2
	0.009	53.2	414±3	329±2	27±2	8±2
$Mg(ClO_4)_2$	—	36.1	441±2	338±2	—	—
	0.001	45.5	422±2	332±2	19±2	6±2
	0.003	51.7	418±2	328±2	23±2	10±2
	0.006	56.2	413±2	327±2	28±2	11±2
	0.009	59.8	410±2	326±2	31±2	12±2

This work was supported in part by the Russian Foundation for Basic Research (grant nos. 04-03-32791 and 05-03-08162) and the Russian Ministry of Science and Education (project no. 02.434.11.2039).

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Received: 10th June 2006; Com. 06/2743