

Research Article

Polymeric Composite Materials for the Detection of Barium Ions in Aqueous Solutions

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The design of polymeric composite materials (PCM) for the optical control of chemical substances is currently one of the actively developing fields of science “at the junction” of polymer, organic, and analytical chemistry. The purpose of this work is the preparation of PCM containing derivatives of crown ethers for the optical determination of barium ions. The polymeric composite materials containing a novel optical molecular sensor have been obtained and investigated on the basis of a number of film-forming polymers. The best results have been obtained for PCM based on polyvinyl butyral films (since the fluorescence and absorption maxima shifted by 9 and 16 nm, respectively) in the fluorescence and absorption spectra of this PCM in the presence of barium ions. This makes the proposed PCM highly promising as sensor elements for the detection of the barium ions in the aqueous solutions.

1. Introduction

The design of polymeric composite materials (PCM) for the optical control of chemical substances is currently one of the actively developing fields of science “at the junction” of polymer, organic, and analytical chemistry [1–3]. One of the widely used approaches for PCM design is the preparation of blend compositions based on a number of necessary components: chromophores and one or more polymers or copolymers depending on the specific applications [4–6]. In addition, the most promising way is to prepare the polymer films a structure of which provides a combination of specific properties [6–8]. There are different polymers discussed in various publications [9–11] which can be used for such film preparations: simple polyvinyl polymers, polyacrylates, polymethacrylates, silicones, cellulose derivatives, etc. The main requirements for film-forming polymers in the case of our systems are the following: high water solubility (before film preparation) and an optimal degree of swelling (after film preparation), reasonable drying time, an optimal ratio between film flexibility and stability, possibility to mix with the most common plasticizers, and an ability to establish

smooth and thin layers. The films prepared must be formed on the optical surface (from which a reliable signal can be obtained) and must have reasonable barrier properties, easy cation penetration to the photosensitive component, wash and/or sweat resistance, etc.

As a photosensitive component in these polymer systems, styryl dyes containing crown-ether groups (which ensure selective binding to the substances to be determined) can be optical molecular sensors (OMS). Such PCM can be promising for the determination of some metal ions. Many of these compounds have been studied by our research team in close cooperation with the Photochemistry Center of the Russian Academy of Sciences [4, 5, 12–16].

An international group of researchers from the Institute of Radiopharmaceutical Cancer Research (Helmholtz-Zentrum Dresden-Rossendorf, Germany) [17] reported recently about the synthesis of the calix[4]crown-6 derivatives modified with either cyclic amide moieties to chelate the barium ions. They measured the stability constants of the complexes between these modified calix[4]crown-6 derivatives and barium ions using NMR and UV/Vis titration techniques [17]. The log K values obtained were in the range

of 4.1-5.0 [17]. The authors [17] found an optimal derivative for barium extraction from the aqueous solutions but did not consider these derivatives for the detection of the barium ions. The Egyptian researchers [18] used anionic dyestuff "Rose Bengal" for barium detection. They claimed developed "sensor for simple, rapid, low cost, and reliable analysis of barium(II) ions in lithophone pigment and in industrial wastewater samples" at level 2.5 mg/L [18] but did not prove it in the practical trials. There are some older works on these topics that have been summarized in our book [19].

It is well known that soluble barium salts are toxic, for example, barium carbonate which is a rat poison. It is important to determine it in aqueous solutions because it can "affect the nervous system, causing cardiac irregularities, tremors, weakness, etc." [20-22].

The purpose of this work is the preparation of polymeric composite materials (which contain photosensitive derivatives of crown ethers) for the optical detection of barium ions.

2. Experimental Part

2.1. Materials. In order to obtain the PCM, a novel azacrown-containing dye OMS (Figure 1) was synthesized in the Photochemistry Center of the Russian Academy of Sciences (Moscow, Russia) by Gromov [4] with the following structure: the dye was obtained by condensation of 1,4-dimethylpyridinium iodide (compound 2) with the formyl N-methylbenzoase-18-crown-6-ether derivative (compound 3) in the presence of pyrrolidine. According to the ^1H NMR spectroscopy data, dye 1 exists as an E-isomer, which follows from the value of the spin-spin interaction constant of the protons of the ethylene fragment $J_{\text{H(a),H(b)}} = 15.9 \text{ Hz}$.

A mixture of 45 mg (0.19 mmol) of 1,4-dimethylpyridinium iodide (compound 2), 2.80 mg (0.23 mmol) of the formyl derivative of N-methylbenzoase-18-crown-6-ether (compound 3), and 3.6 ml of abs. EtOH and 0.04 ml of pyrrolidine (Scheme 1) were heated in an oil bath at 80°C for 25 hours. The reaction mixture was evaporated in vacuum, extracted with hot benzene to remove unreacted compound 3. The residue was dried in air, and dark red crystals were received in the amount of 59 mg (54%). Melting temperature was $163\text{-}164^\circ\text{C}$. The data of the ^1H -NMR spectrum (Bruker DRX500, DMSO- d_6 , 23°C) were the following: 2.90 (s, 3 H, MeN), 3.41 (t, 2 H, NCH₂CH₂O, $J = 6.0$), 3.54 (m, 4 H, 2 CH₂O), 3.55 (m, 4 H, 2 CH₂O), 3.62 (m, 4H, 2 CH₂O), 3.72 (t, 2 H, NCH₂CH₂O, $J = 6.0$), 3.85 (m, 2H, CH₂CH₂OAr), 4.17 (m, 2H, CH₂OAr), 4.20 (s, 3 H, MeN +), 6.86 (d, 1 H, H (17), $J = 8.5$), 7.22 (dd, 1H, H (18), $J = 8.5$, $J = 1.4$); 7.30 (broad s, 1 H, H (20)), 7.32 (d, 1 H, CH (a) = CH (b), $3J_{\text{trans}} = 15.9 \text{ Hz}$), 7.91 (d, 1N, CH (a) = CH (b), $3J_{\text{trans}} = 15.9 \text{ Hz}$), 8.08 (d, 2H, H (3), H (5), $J = 6.6$), and 8.75 (d, 2H, H (2), H (6), $J = 6.6$). Found (%): C, 52.86; H, 6.03; N, 4.74. For $\text{C}_{25}\text{H}_{35}\text{IN}_2\text{O}_5$, it is calculated, %: C, 52.64; H, 6.18; N, 4.91.

For the PCM preparation, the following polymers (Aldrich, USA) were used: cellulose acetate hydrophthalate (CAHP), cellulose acetate butyrate (CAB), polyvinyl butyral (PVB), and polyvinyl chloride (PVC). A commercially

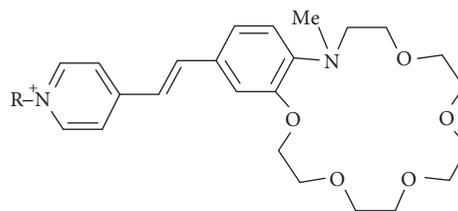


FIGURE 1: Chemical structure of the azacrown-containing dye OMS [4].

available plasticizer (Aldrich, USA), dioctyl sebacic acid (DSA), was used in the mixtures with the abovementioned polymers.

The following solvents (Chimmed, Russia) such as chloroform, acetonitrile, dichloroethane, tetrahydrofuran were used. Barium perchlorate $\text{Ba}(\text{ClO}_4)_2$ (99% from Aldrich, USA) and bidistilled water were used for the preparation of the "analyte" solutions.

2.2. Methods. First, the suitable solvents were found for polymer solution preparations. The optimal conditions were the following: 4% polymer solution of CAB or CAHP in acetonitrile, PVB in dichloroethane, and PVC in tetrahydrofuran. Second, the appropriate amount of OMS solution in chloroform (in the case of PVB or PVC) or acetonitrile (in the case of PVB or PVC) was added to the abovementioned polymer solutions.

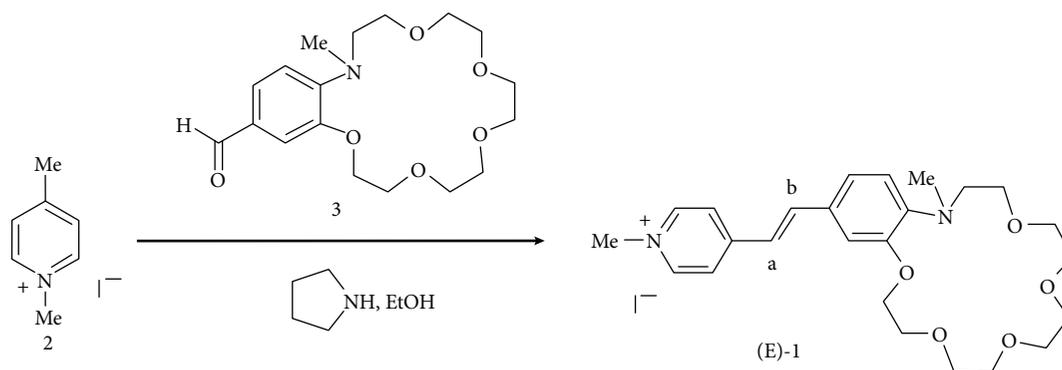
From the solutions prepared, thin films were deposited onto quartz substrates (to have the possibility to measure absorption and fluorescence spectrum). Quartz glasses were placed on a special horizontal table at an adjustable level. On the glass with a pipette, a polymer solution was spread dropwise over the entire glass area. The membrane was cast and dried for 24 hours at room temperature in solvent vapors. The thickness of the membranes calculated was about $10 \mu\text{m}$. The content of OMS in the membrane was about 1% of the weight of the polymer.

Absorption and fluorescence spectra were obtained on a Hitachi 330 and Shimadzu RF 5000 using quartz glasses (for films) and quartz cuvettes (for solutions). In the film and solution, in the presence of OMS, a marked peak was observed, the maximum of which was observed at the corresponding wavelength.

Then the films containing OMS were exposed to the aqueous solutions of salts for 10 minutes. Afterwards, the absorption and fluorescence spectra were recorded, and changes in the wavelength of the absorption or fluorescence maximum were noted. Statistical analysis was fulfilled using the standard packages of "STATISTICA 7" (StatSoft, USA) and "OriginPro 8" (OriginLab, USA).

3. Results and Discussion

First, the screening procedure for about 10 polymers (polyvinyl polymers, polyacrylates, polymethacrylates, cellulose derivatives, etc.) was carried out in order to find the most suitable compound for OMS immobilization.



SCHEME 1: Synthesis route of the dye OMS: iodide 1-methyl-4 - [(E) -2- (16-methyl-2,3,5,6,8,9,11,12,15,16-decahydro-14H-1,4,7,10,13,16-benzopentaazaazacyclooctadecine-19-yl) -vinyl] pyridinium (compound 1) using 1,4-dimethylpyridinium iodide (compound 2), N-methylbenzoase-18-crown-6-ether (compound 3), etc. (synthesized in the Photochemistry Center of the Russian Academy of Sciences by Gromov [4]).

The transparency of the polymer film before and after the OMS introduction (for the possibility of carrying out spectral studies) was the major criteria of the polymer selection. The following polymers were preliminarily investigated for the possibility of film formation: PVB, CAB, CAHP, PVC, polymethyl methacrylate (PMMA), copolymer of methylmethacrylate and ethyl acrylate (PMMA + EA), polystyrene (PSt), copolymer of polystyrene and methyl acrylate (PSt + MA), copolymer of polystyrene and methyl methacrylate (PSt + MMA), and polyvinylalcohol (PVA). All samples of PMMA and PSt films were very brittle, whereas PVA films, PSt + MA, PSt + MMA, and PMMA + EA copolymer films were turbid. Therefore, four types of polymers (PVB, CAB, CAHP, or PVC) were chosen that had a reasonable combination of all desirable properties. The novel OMS was completely and evenly (randomly) distributed in all these polymers as a structural matrix for PCM. After such preliminary experiments, the fluorescence spectra of OMS (Figure 2) introduced into the polymer matrices (based on PVB, CAB, CAHP, or PVC) were studied before and after the action of the analyte (solutions of barium perchlorates with the concentration of 10^{-6} - 10^{-3} mol/L).

The results of the relative changes of the fluorescence maxima in the spectra for various PCMs are presented in Table 1.

Table 1 shows that the positions of the fluorescence maximum for OMS in polymer films are fairly close for PVB, PVC, and CAB (592-595 nm) and differ significantly from the λ_{\max} position for OMS in CAHP films (564 nm). This indicates the OMS and polymer interaction in the latter case. When the barium salt is applied to the polymeric films containing OMS, the absorption maximum shifts for all the PCM to the long-wavelength region of the spectrum. The largest shifts of λ_{\max} after adding barium perchlorate to solutions are observed for PCM based on PVB and CAHP.

It is assumed that OMS is presented in polymer films in the form of "head-to-tail" dimers formed during the electrostatic interaction of the crown-ether cycle and the pyridine part of the two closely packed OMS molecule. An interaction of OMS dimers with barium occurs ineffectively; a shift of

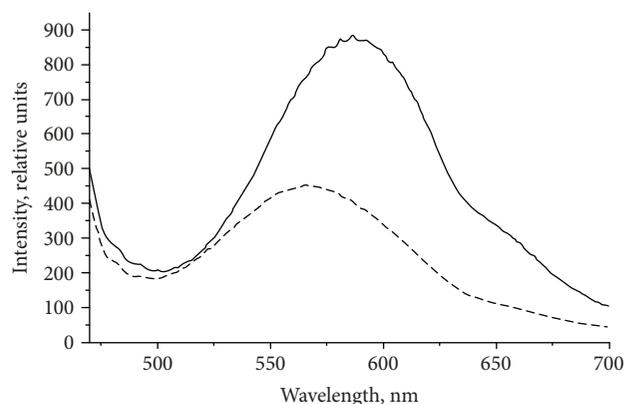


FIGURE 2: Fluorescence spectra of OMS in the CAGF film before (dashed line) and after (solid line) incubation in the 10^{-3} M $\text{Ba}(\text{ClO}_4)_2$ solution.

TABLE 1: The wavelength of the fluorescence maximum for PCM with OMS before and after incubation with $\text{Ba}(\text{ClO}_4)_2$.

Spectral characteristics	PVB	PVC	CAHP	CAB
λ_0 (before exposure), nm	592 ± 1	595 ± 1	564 ± 1	592 ± 1
λ_1 (after exposure), nm	601 ± 1	598 ± 1	586 ± 1	593 ± 1
$\Delta\lambda$, nm	+9	+3	+22	+1

3 nm is observed in the case of PVC, which is a little bit higher than those in the case of a commercially available plasticizer (DSA) used without OMS. In the case of PVB, the shift is 9 nm which can be explained by the decay of some part of the OMS dimers due to their interaction with barium ions penetrating in the PVB matrix.

The interaction of CAHP carboxyl groups with charged pyridine part of the OMS molecule leads to the dissociation of the OMS dimeric form up to individual OMS molecules. Therefore, in the case of CAHP, the interaction of OMS with the barium ions is more efficient and accompanied by almost

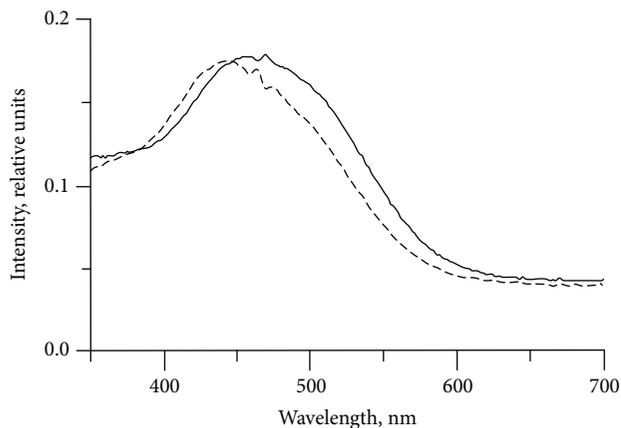


FIGURE 3: Absorbance spectra of OMS in the PVB film before (dashed line) and after (solid line) incubation in the 10^{-3} M $\text{Ba}(\text{ClO}_4)_2$.

TABLE 2: The wavelength of the absorbance maximum for PCM with OMS before and after incubation with $\text{Ba}(\text{ClO}_4)_2$.

Spectral characteristics	PVB	PVC	CAHP	CAB
λ_0 (before exposure), nm	448 ± 1	447 ± 1	450 ± 1	453 ± 1
λ_1 (after exposure), nm	464 ± 1	450 ± 1	462 ± 1	456 ± 1
$\Delta\lambda$, nm	+16	+3	+12	+3

twofold increase in the fluorescence intensity (Figure 2). In this case, the shift of the maximum of fluorescence is the greatest (about 22 nm).

Then, the absorption spectra of OMS (Figure 3) introduced into a polymer matrix based on PVB, CAB, PVC, or CAHP were studied before and after the action of the “analytes” (solutions of barium perchlorate, with the concentration of 10^{-6} to 10^{-3} mol/L).

The results of the absorption spectra for various PCMs are presented in Table 2.

Table 2 shows that for the PCM based on PVC and CAB, the shift in the absorption maximum is insignificant. The largest shifts of the absorption maximum are observed in the polymer films based on PVB (Figure 3) and CAHP. An important advantage of these films is the dependence of the magnitude of the absorbance maximum shift vs. $\text{Ba}(\text{ClO}_4)_2$ concentration (Table 3).

The large shifts observed in the absorption maximum and the dependence of the shift amount on the concentration of barium cations make the proposed composition as the most promising for the preparation of optical chemosensors for Ba^{2+} ions.

4. Conclusions

Thus, polymeric composite materials containing a novel optical molecular sensor have been obtained and investigated on the basis of a number of film-forming polymers. The best results have been obtained for PCM based on polyvinyl butyral films since the fluorescence and absorption maxima

TABLE 3: Wavelength of the absorbance maximum for NCM with OMS in the PVB film at various concentrations $\text{Ba}(\text{ClO}_4)_2$.

Ba^{2+} concentration mol/L	λ_0 , nm, (before impregnation)	λ_1 , nm, (after impregnation)	Relative shift $\Delta\lambda$, nm
$C = 10^{-3}$	447 ± 2	463 ± 2	+16
$C = 10^{-4}$	447 ± 2	462 ± 2	+15
$C = 10^{-5}$	447 ± 2	461 ± 2	+14
$C = 10^{-6}$	447 ± 2	459 ± 2	+12

shifted by 9 and 16 nm, respectively (in the fluorescence and absorption spectra of this PCM by addition of barium ions). This makes the proposed PCM highly promising as materials for possible detection of the barium ions in aqueous solutions.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interests regarding the publication of this paper.

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References

- [1] J.-M. Lehn, “Beyond chemical synthesis: self-organization?!” *Israel Journal of Chemistry*, vol. 58, no. 1-2, pp. 136–141, 2018.
- [2] J.-M. Lehn, “Perspectives in chemistry, aspects of adaptive chemistry and materials,” *Angewandte Chemie International Edition*, vol. 54, no. 11, pp. 3276–3289, 2015.
- [3] J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, John Wiley & Sons Ltd, Chichester, England, 2000.
- [4] S. P. Gromov, MIPT, Moscow, Russia, 2002.
- [5] E. N. Ushakov, M. V. Alifimov, and S. P. Gromov, “Design principles for optical molecular sensors and photocontrolled receptors based on crown ethers,” *Russian Chemical Reviews*, vol. 77, no. 1, pp. 39–58, 2008.
- [6] S. Y. Zaitsev, D. O. Solovyeva, and I. S. Zaitsev, “Multi-functional membranes based on photosensitive crown-ether derivatives with advanced properties,” *Advances in Colloid and Interface Science*, vol. 222, pp. 755–764, 2015.
- [7] S. Y. Zaitsev, *Supramolecular Nanodimension Systems at the Phase Interface: Concepts and Prospects for Bio-Nanotechnologies*, LENAND, Moscow, Russia, 2010.

- [8] S. Y. Zaitsev, "Membrane nanostructures based on biologically active compounds for biotechnology," *Nanotechnologies in Russia*, vol. 4, no. 7-8, pp. 44-55, 2009.
- [9] F. N. Jones, M. E. Nichols, and S. P. Pappas, *Organic Coatings, Science and Technology*, John Wiley & Sons, Inc., 4th edition, 2017.
- [10] A. Das, G. Vantomme, A. J. Markvoort et al., "Supramolecular copolymers: structure and composition revealed by theoretical modeling," *Journal of the American Chemical Society*, vol. 139, no. 20, pp. 7036-7044, 2017.
- [11] J. M. Lehn, "Dynamers: from supramolecular polymers to adaptive dynamic polymers," in *Hierarchical Macromolecular Structures: 60 Years after the Staudinger Nobel Prize I*, Advances in Polymer Science, pp. 155-172, Springer, 2013.
- [12] S. Y. Zaitsev, E. N. Zarudnaya, D. Möbius et al., "Ultrathin chemosensing films with a photosensitive bis(crown ether) derivative," *Mendeleev Communications*, vol. 18, no. 5, pp. 270-272, 2008.
- [13] A. A. Turshatov, D. Möbius, M. L. Bossi et al., "Molecular organization of an amphiphilic styryl pyridinium dye in monolayers at the air/water interface in the presence of various anions," *Langmuir*, vol. 22, no. 4, pp. 1571-1579, 2006.
- [14] M. L. Bossi, A. A. Turshatov, S. Y. Zaitsev, M. V. Alfimov, D. Möbius, and S. W. Hell, "Influence of monolayer state on spectroscopy and photoisomerization of an amphiphilic styryl-pyridinium dye on a solid substrate," *Langmuir*, vol. 23, no. 7, pp. 3699-3705, 2007.
- [15] S. Y. Zaitsev, V. V. Bondarenko, M. S. Tsarkova et al., "Polymer composite materials with photosensitive bis-crown-ether dye," *Polymer Research Journal*, vol. 4, no. 1, pp. 11-16, 2011.
- [16] S. Y. Zaitsev, E. N. Zarudnaya, I. S. Zaitsev et al., "Thin films with immobilized bis-crown-ether dye," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 383, no. 1-3, pp. 120-124, 2011.
- [17] J. Steinberg, D. Bauer, F. Reissig, M. Köckerling, H.-J. Pietzsch, and C. Mamat, "Modified calix [4] crowns as molecular receptors for barium," *ChemistryOpen*, vol. 7, no. 6, pp. 432-438, 2018.
- [18] A. M. Othman, M. S. El-Shahawi, and M. Abdel-Azeem, "A novel barium polymeric membrane sensor for selective determination of barium and sulphate ions based on the complex ion associate barium(II)-rose bengal as neutral ionophore," *Analytica Chimica Acta*, vol. 555, no. 2, pp. 322-328, 2006.
- [19] S. Y. Zaitsev, *Supramolecular Systems at the Interface of Phases as Models of Biomembranes and Nanomaterials*, Moscow: Nord Computer, Donetsk, Ukraine, 2006.
- [20] J. W. Moore, *Inorganic Contaminants of Surface Waters, Research and Monitoring Priorities*, Springer, New York, NY, USA, 1991.
- [21] <http://www.espimetals.com/index.php/msds/46-barium>.
- [22] P. Patnaik, *Handbook of Inorganic Chemicals*, McGraw-Hill, New York, NY, USA, 2003.



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