16th International Scientific Conference "Chemistry and Chemical Engineering in XXI century" dedicated to Professor L.P. Kulyov, CCE 2015

Effect of Polyethylene Glycol Immobilized into a Polymethacrylate Matrix on the Sorption of Rhodamine

M.A. Gavrilenko[a]*, E.A. Gazieva[b], N.A. Gavrilenko[b], I.V. Kirsanova[a]

[a]*Tomsk Polytechnic University, 30, Lenin ave,. Tomsk, 634050, Russia*
[b]*Tomsk State University, 36, Lenin ave., Tomsk, 634050, Russia*

Abstract

Combined matrix PMMA and PEG, having a polymethacrylate backbone and hydrophilic PEG chains, has been synthesized and applied for the design of transparent colour sensors. Introduction of the hydrophilic PEG chains in the PMMA bulk overcomes the limitations caused by the hydrophobicity of PMMA, and exhibits good wettability, stable and specific adsorption. We suppose that the adsorption of rhodamine on such networks depends on the chemical composition of the system and describes the interaction of the xanthene dye with the polymers.

1. Introduction

Poly(methyl methacrylate) (PMMA), one of the commonly used polymers, is widely used to fabricate optical analytic systems. There have been advantages for the application of PMMA in analysis due to such properties as hydrophobicity and compatibility with additives. Bulk modification is an effective way to improve the analytical properties while retaining the transparent properties of the polymer. Various modifications of the PMMA matrix have been obtained using different techniques like physical adsorption, biomolecule adsorption, chemical

---

* Corresponding author. Tel.: +7-322-293-6444
E-mail address: dce@mail.ru

modification and so on[1-3]. PMMA have unique advantages over other polymers, for their physical and chemical properties can be easily changed by molecular design.

The introduction of polyethylene glycol (PEG) into the PMMA has attracted considerable attention as a means of minimizing waste sorption, because of their low interfacial energy, non-adhesive property and high diffusion. The technique was described[4] where PEG was immobilized into polymethylmethacrylate matrix (PMM) on polymerization stage.

Combined matrix PMMA and PEG, having a polymethacrylate backbone and hydrophilic PEG chains, has been synthesized and applied for the design of transparent color sensors. The properties of the new modified PMM such as attachment, functionality, and sorption properties are characterized by various techniques.

The results of investigation of xanthene dyes sorption into transparent matrix are used in the field of technology for sensors, catalysis, analytical chemistry and drug discovery. Last but not least xanthene dyes sorption is of utmost importance for the monitoring of oil fields. A large number of experimental studies of xanthene dyes sorption to various sorbents have been performed in order to understand the underlying mechanism of the sorption process[5-7]. In this study, the results of xanthene dyes sorption on PMMA-PEG polymer are presented. This simple method allows the study of a wide range of PMMA-PEG polymers with well-defined the optical sensor properties. The obtained polymers were exposed to solutions containing rhodamine and the amount of sorbed substance was measured.

2. Material and Methods

PEG and methyl ether methacrylate (MMA) purchased from Aldrich, was used as received. All of other chemicals were of analytical grade and purchased from Shanghai Chemical Reagent Co. (Shanghai, China). PMMA was synthesized via free radical block polymerization, using benzoyl peroxide as initiator. Typically, 50 g MMA and 1-10 g PEG reacted at 60-70 °C for 4 h with benzoyl peroxide at a concentration of 0.0005 $g \cdot L^{-1}$ in 100 ml without solvent. Then these plates were cut as $6.0^x 8.0$ mm (weight 0.05 g) intended for analyses.

The dye used in this study is rhodamine, which is anionic in nature (purity: 98.7%, color: red, A_{max}: 530 nm). The structure of the dye is shown in Fig. 1. The solutions of $2.0^x 10^{-3}$ $mol \cdot L^{-1}$ rhodamine were prepared by dissolving precise loads in water.
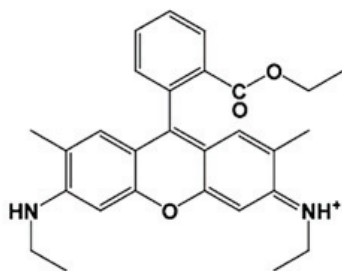

Fig. 1. Structure of rhodamine

Colorimetric scales were obtained using 1 $mg \cdot mL^{-1}$ of the following certified reference materials produced by Ekoanalitika Ltd., Russia. The required pH was adjusted using acid (sulfuric acid, nitric acid, phosphoric acid) and sodium hydroxide. Photometric method was used to evaluate of rhodamine adsorption on the PMMA plates. To observe the specific adsorption, modified PMMA-PEG was introduced into the solution of rhodamine 2 $mg \cdot mL^{-1}$, pH 7.0 for 10 min without washing. Analytical peak was displayed at the excitation of 530-540 nm. Immobilization of analytical reagents into a polymeric matrix has been carried out in a static mode. The solution was placed in a constant temperature bath and stirred with the help of a stirrer at 120 rpm.

3. Result and Discussion

Spectra and structure PMMA-PEG are presented (Fig. 2, 3) The spectrum contains the characteristic absorption band for O–C=O stretch ($v = 1727$ cm^{-1}), attributable to the ester groups in the PMMA polymer, and the band for C–O stretch ($v \approx 1100$ cm^{-1}), attributable to the ether groups of PEG. The spectrum contains the characteristic band for carboxyl group (O–C=O) stretch ($v = 1727$ cm^{-1}), attributable to the ester groups in the PMMA polymer, and there is no absorption around 1100 cm−1. The IR results indicate that PEG has been successfully deposited onto the PMM by the anchoring of MMA segments[8]. The IR spectroscopic results confirm the presence of both PEG and PMMA active fragments in the transparent matrix.
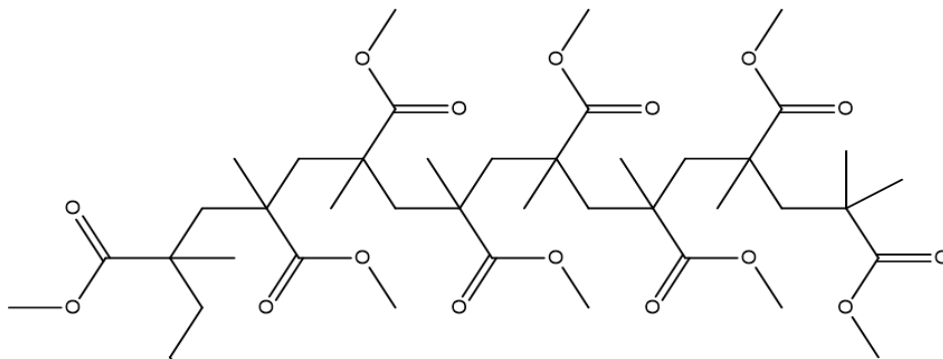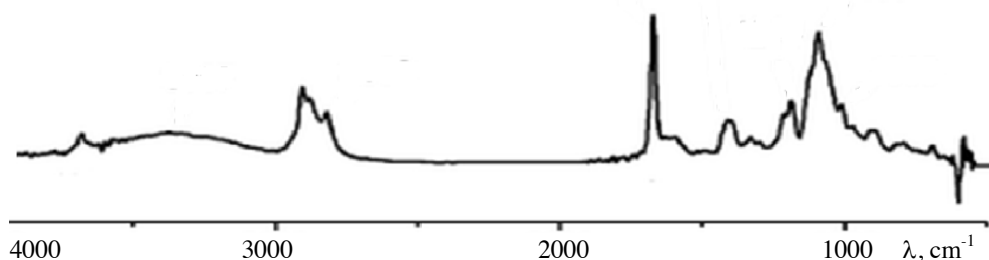
Fig. 2. Structure of the PEG-PMMA matrix.

Fig. 3. FTIR spectra of the PEG-PMMA matrix.

In the case an initial PMM, rhodamine adsorption is frequently observed, however, the results vary and the exact values of the adsorbed amounts are difficult to reproduce. A possible explanation for this is that generally adsorption is weak due to the low surface energy. Though the interaction of rhodamine and PMM is not very favorable, neither is the interaction between water and dyes. The increase of specific adsorption of the PMMA-PEG could be mainly attributed to the flexible hydrophilic PEG chains in the bulk and them contacts with sorbate into the aqueous solution. PEG chains will increase the surface energy and mediate in a second step the adsorption of xanthene dyes into volume of PMM. The increase in surface energy is quite visible in a decrease of the dyes contact observed during analytical determination. Absorbance spectra of PMMA-PEG matrix after the sorption of rhodamine are depicted in Fig. 4 .
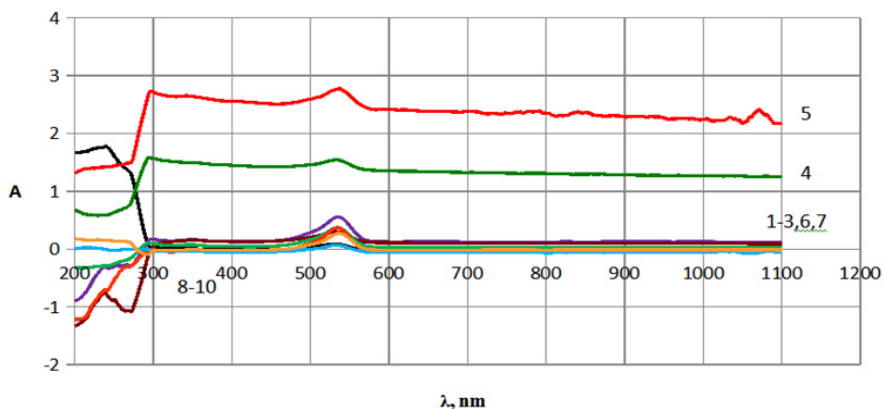
Fig. 4. Rhodamine absorption spectra for different compositions of the polymer (A – degree of transparence; number corresponds to the amount of PEG, %) at a concentration of rhodamine 0.6 mg·L-1

It can be clearly seen that the minima of the absorbance of the polymer layer after rhodamine exposure for the sample with >10 % PEG. All the spectra are offset vertically for clarity. The upper spectrum shows the absorbance of rhodamine by a polymer with 5% PEG. Between 8 and 10 % of PEG the transparence degree drops with increasing of adsorbed rhodamine. Samples fragments of spectrum below abscissa demonstrated a milkiness of polymer plates and were excluded from further experimentation. Stable strong signal was detected in samples with 5 % PEG. Changing of the structure after the addition of PEG confirmed micrographs of the PMMA-PEG surface. These changes found evidence particularly at the 5% PEG. Areas with increased availability of diffusion can be seen in Fig. 5.
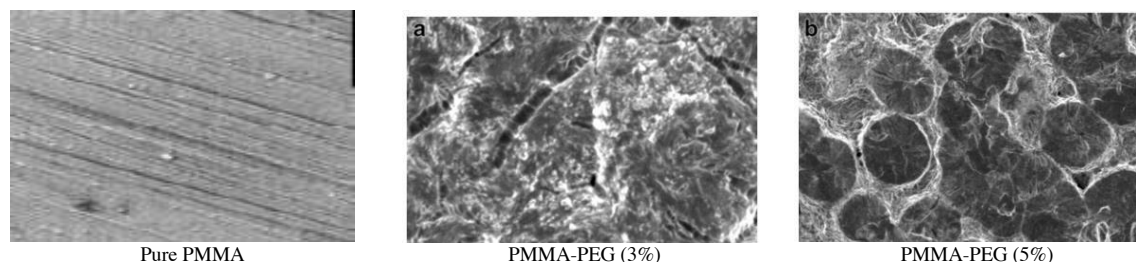

| Pure PMMA | PMMA-PEG (3%) | PMMA-PEG (5%) |

Fig. 5. Micrographs of the PMMA-PEG surface

With increasing length of the PEG side chains the polymer becomes more hydrophilic and the transparence of the polymer in the aqueous solution increases Thus short chains of PEG allow and long chains of PMMA prevent the rhodamine adsorption, which is consistent with the results for similar structures from the literature [9]. The polymer matrix with 5 % PEG saved the high transparency and the ability of rhodamine adsorption. Analytical determination of rhodamine was carry out using this matrix hereinafter. Results are included in Table 1.

Table 1. The results of determination of rhodamine in aqueous solution by independent method

Method	Added, mg·L^{-1}	Found, mg·L^{-1}	Sr	σ,%
Photometric method	0.70	0.77±0.11	0.09	110
HPLC	0.70	0.72±0.04	0.04	103

Calculations were performed with a calibration function for a pure substance. The samples were then purified from impurities of n-heptane and further determining dye was performed by fluorimetry[10]. According to comparison results of analyzes carried out shows that solid phase extraction rhodamine into the PMMA-PEG matrix allows determination of rhodamine with high accuracy.

Rhodamine fluorescence maxima are shifted to longer wavelengths from $\lambda = 552$ nm to 586 nm see. In the fluorescence analysis using polymer plates as sensors has been identified the most optimal variant spectral measurements at an angle 45 °C in the measuring cell. The highest intensity of fluorescence from the samples is achieved with the position of the sensor.

When the adsorption of rhodamine into PMMA-PEG is considered, the chemical composition of the matrix material would only be important if the dye could penetrate deep down into the polymer bulk[11]. If the polymer is small swollen in the water, the free energy of the adsorption process will depend on how the xanthene dye is able to interact with the short chains of PEG. The free energy of the adsorption process contains an enthalpic component $\Delta G = \Delta H - T\Delta S$.

The interaction between the rhodamine and PMMA-PEG polymer is strong due to the strong contribution of the enthalpic term after interaction with side chain of PEG. The situation completely changes when the interaction between dye and polymer is weak and accordingly the enthalpy of the adsorption process is small or almost zero (for the initial PMMA case). In this case, the entropy component of the free energy of the adsorption process will determine whether xanthene dyes adsorption occurs or not provided that the size of the xanthene dyes is somewhat

smaller than the mesh size of the polymer matrix. When the rhodamine is very large compared to the mesh size of the polymer matrix, additional size exclusion effects need to be considered[12].

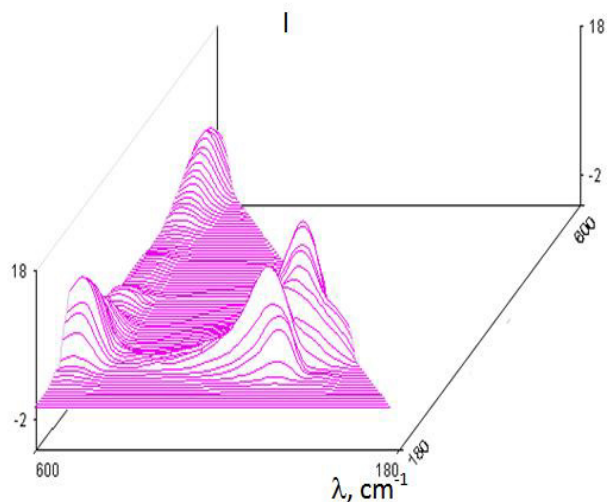Fig. 6. The maximum fluorescence of rhodamine into PMMA-PEG (5%) matrix

Fig. 7. Three-dimensional spectrum of rhodamine into with concentration 8 µg·L^{-1} PMMA-PEG (5%) matrix

One is the entropy of mixing, which favors an even distribution of molecules in the polymer matrix and thus favors also the presence of the rhodamine in the polymer bulk. When a polymer–rhodamine system is viewed, the change in entropy due to mixing is expected to be rather small, especially since many (small) water molecules are replaced by the other molecule, which reduces the entropy[13]. The details of the entropy of mixing will depend on the size and conformational rigidity, also segment density of the polymer.

The other contribution is the entropy of conformation of the PEG chains, where the addition of more material to the layer enhances the segment–segment interactions and/or the osmotic pressure of rhodamine and the corresponding counter ions, which in turn forces the polymer molecules to stretch away from the surface. This additional stretching leads to a strong reduction of the entropy of conformation[14]. If this loss of entropy due to the conformational changes is larger than the gain of entropy due to mixing, the net entropy change is negative, which leads to a positive free energy of the adsorption process, all based on the assumption that the enthalpy of the mixing process is almost zero.

4. Conclusion

In this study we investigated the rhodamine adsorption into PEG-PMMA. The PEG in the polymethacrylate backbone are achieved by the immobilization. Introduction of the hydrophilic PEG chains in the PMMA bulk overcomes the limitations caused by the hydrophobicity of PMMA, and exhibits good wettability, stable and specific adsorption. We propose that the adsorption of rhodamine on such networks depends on two parameters. One describes the interaction of the xanthene dyes with the polymers and depends largely on the chemical composition of the system. Second, if the enthalpic contribution is large, xanthene dye adsorption is strong. If the enthalpy of the adsorption process is close to zero, not so much the chemical composition, but rather a small set of physical parameters of PEG dominate the sorption process.

Acknowledgements

References

1. McDonagh C., Burke C.S., MacCraith B.D. Optical chemical sensors. *Chem Rev*. 2008; **108**:400–422.
2. Gavrilenko M.A., Gavrilenko N.A., Mokrousov G.M. Preconcentration of phenols on a polymethacrylate sorbent for their gas-chromatographic determination in water. *J. Analytical Chemistry* 2006; **61**: 216-218.
3. Han W., Yamauchi M., Hasegawa U., Noda M., Fukui K., van der Vlies A.J., Uchiyama S., Uyama H. Pepsin immobilization on an aldehyde-modified polymethacrylate monolith and its application for protein analysis. *J. Bioscience and Bioengineering* 2015; V119, **5**: 505-510.
4. Gavrilenko, N.A., Mokrousov, G.M. The indicator sensitive material for determination of microquantities of substances. Patent 2272284 (RU); 2004.
5. Chiang T.-L., Wang Y.-C., Ding W.-H. Trace determination of rhodamine B and rhodamine 6G dyes in aqueous samples by solid-phase extraction and high-performance liquid chromatography coupled with fluorescence detection. *J. Chin. Chem. Soc*. 2012; **59**: 515-519.
6. Desiderio C., Marra C., Fanali S. Quantitative analysis of synthetic dyes in lipstick by micellar electrokinetic capillary chromatography. *Electrophoresis* 1998; **8-9**: 1478-1483.
7. Gavrilenko M.A., Gavrilenko N.A., Amerkhanova S.K., Uali A.S., Bilyalov A.A. Trace Determination of Rhodamine and Eosine in Oil-Water Reservoir Using Solid-Phase Extraction. *Advanced Materials Research*, 2014; **880**: 276-281.
8. Narayanaswamy R., Wolfbeis O.S. Optical sensors: Industrial, Environmental and Diagnostic Applications. *Springer*; 2004.
9. Vakhonina T.A., Ivanova N.V., Smirnov N.N., Yakimansky A.V., Balakina M. Yu., Sinyashin O. G. Nonlinear-optical properties of methacrylic (co)polymer with azo chromophores in the side chain. *Mendeleev Communications* 2014; **204**: 138-139.
10. Kim H.N., Guo Z., Zhu W., Yoon J., Tian H. Recent progress on polymer-based fluorescent and colorimetric chemosensors. *Chem. Soc. Rev*. 2011; **40**: 79-93.
11. Gavrilenko M.A., Gavrilenko N.A., Burmetieva M.S. Sorption of rhodamine into polymer block matrix. *Advanced materials research* 2014; **1040**: 437-441.
12. Mcheik A. H., El Jamal M. M. Kinetic study of the discoloration of rhodamine B with persulfate, iron activation. *J. Chemical Technology and Metallurgy* 2013; **48**: 357-365.
13. Huang J.-H., Huang K.-L., Liu S.-Q., Wang A.T., Yan C. Adsorption of rhodamine B and methyl orange on a hypercrosslinked polymeric adsorbent in aqueous solution. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 2008; 330: 55-61.
14. Huang J.-H., Huang K.-L., Liu S.-Q., Luo S.Y., Shi S.Y. Synthesis, characterization, and adsorption behavior of aniline modified polystyrene resin for phenol in hexane and in aqueous solution. *J. Colloid Interface Sci*. 2008; **317**: 434-441.