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Branched poly-*N*-vinyl-2-pyrrolidones as polymeric nanocontainers for hydrophilic dyes

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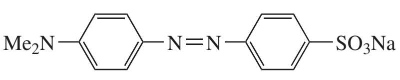
The capability of *N*-vinyl-2-pyrrolidone branched copolymers to incapsulate molecules of hydrophilic dyes has been found and studied.

The preparation of functional nanosized materials – polymeric nanocontainers (host) capable of incorporating and retaining molecules of low-molecular compounds (guests) such as catalysts, bioactive compounds and drugs by noncovalent binding (van der Waals interactions, hydrogen bonds) – is of considerable interest.[1,2] Compounds of this kind include branched polymers incorporating terminal chains in peripheral layers and, in comparison with linear polymers, containing excessive free volume owing to their architecture; such a free volume exists as cavities of various sizes.

The aim of this work was to study the host–guest immobilization of ionic hydrophilic dyes (methyl orange **1**, rose bengal **2** and methylene blue **3**) inside macromolecules using a branched copolymer of *N*-vinyl-2-pyrrolidone (NVP) with triethylene glycol dimethacrylate as an example of such macromolecules.

The branched copolymer was obtained by one-stage radical copolymerization of NVP with triethylene glycol dimethacrylate (TEGDMA) in ethanol controlled by a chain transfer agent, 1-decanethiol (DT), in the ratio NVP:TEGDMA:DT = 100:20:20 (mol%) using a method reported previously.[3] The copolymer is soluble in organic solvents, such as alcohols and chloroform, but insoluble in water. The presence of dimethacrylate units in the copolymer was confirmed by IR spectroscopy: in addition to the absorption band of the lactame C=O stretching vibrations at 1680 cm^{-1}, the IR spectra contain an absorption band of TEGDMA C=O stretching vibrations at 1725 cm^{-1}. According to ozonolysis data, the content of non-reacted dimethacrylate C=C bonds in the copolymer was 0.9×10^{-3} mol of double bonds per gram of the compound. Thus, the copolymer macromolecules consist of hydrophilic (NVP units) and hydrophobic (TEGDMA units and $C_{10}H_{21}S$ groups incorporated in polymeric chains due to chain transfer) components, which differ in thermodynamic compatibility and solubility. The diphilic nature of NVP copolymer macromolecules allows them to be considered as non-ionic surfactants.



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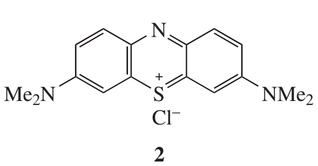

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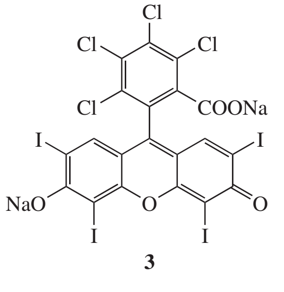

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The molecular-mass distribution of the copolymer was measured by size-exclusion chromatography using a Waters GPCV 2000 liquid chromatograph combined with light scattering (WYATT DAWN Helios II) detector. *N*-Methylpyrrolidone containing LiCl was used as the eluent. The elution rate was 1 ml min^{-1}. The measurement temperature was 70 °C. The refractive index d*n*/d*c* is 0.074 ml g^{-1}. The molecular mass characteristics of the copolymer were as follows: $M_w = 19.7\times10^3$, $M_w/M_n = 2.3$.

The branched structure of the copolymer follows from its rheological properties measured in isopropanol. The copolymer has low intrinsic viscosity $[\eta] = 0.1$ dl g^{-1} and a weaker dependence of reduced viscosity on concentration in comparison with the linear polymer: the slope is 0.4×10^{-2}. For the linear polymer ($M_w = 63\times10^3$, $M_w/M_n = 2.2$) intrinsic viscosity $[\eta] = 0.34$ dl g^{-1}, the slope of dependence of reduced viscosity on concentration is 6.9×10^{-2}. These facts suggest a more compact conformation (higher molecular packing density) of its macromolecules in comparison with the linear polymer.

The branched structure of the NVP copolymer and, hence, the existence of excessive free space as cavities with various sizes creates prerequisites for immobilizing dye molecules inside the macromolecules.[4,5] The fact that the copolymer loses solubility in water when branching methacrylic units and DT residues in the form of $C_{10}H_{21}$ alkyl substituents are incorporated makes it possible to use joint mechanical activation of the solutions of dyes **1**–**3** in water and branched copolymer in chloroform for this purpose.

To immobilize dyes in copolymers, a solution of a dye in water (2 ml; $[C]_0 = 2\times10^{-4}$ mol dm^{-3}) was added to a solution of the copolymer in chloroform (4 ml, 7 g dm^{-3}), and the mixture was stirred at 20 °C with a magnetic stirrer. On mixing an aqueous solution of a dye and a polymer solution in chloroform, the macromolecules form direct micelle type associates at the interface of the two phases owing to their diphilic nature; the molecules of **1**–**3** are localised in the hydrophilic part of these associates. After that, the mixtures were allowed to settle until complete separation of the phases. The lower layer, that is,

Table 1 Main physicochemical parameters of dyes **1**–**3** and the results of their immobilization in a branched copolymer.

Dye	Molecular mass	Van der Waals volume of the molecule,[a] Å^3	Type of charged species in water	Amount of the dye transferred into the copolymer (%)	Specific sorption, mmol g^{-1}
1	327.24	247.3	zwitter-ion	42.7	6.1×10^{-3}
2	1017.65	446.7	anion (An$^-$)	63.2[b]	9.2×10^{-3}
3	319.86	254.6	cation (Ct$^+$)	76.0[b]	10.9×10^{-3}

[a] The calculations for the molecular forms of dyes **1**–**3** were carried out using the Chem 3D software. [b] The calculation was based on the total contents of the dye monomer and dimer in the aqueous solution.

a solution of the copolymer in chloroform, became coloured. The upper layer, that is, a solution of the dye in water, was isolated, and its absorption spectrum was recorded in the visible range using a Specord M40 spectrophotometer. The optical density D was determined in the maxima of the corresponding absorption bands of dyes **1**–**3** in aqueous solution after dye immobilization and the percentage of the dye immobilized in the copolymer was calculated. Specific sorption was calculated[6] using the formula $a = (C_0 - C_x)V/m$, where C_0 and C_x are the dye concentrations in the aqueous solution before and after the immobilization, respectively; V is the volume of the aqueous solution (dm^3); and m is the polymer mass (g).

Table 1 shows the results on the sorption of dyes **1**–**3** by the branched copolymer. The branched copolymer absorbs above 40, 60 and 70% of dyes **1**–**3**, respectively, from the aqueous solution; the adsorption is $\sim2\times10^{-3}$, $\sim9\times10^{-3}$ and 3.5×10^{-3} g of dyes **1**–**3**, respectively, per gram of the copolymer. Thus, anionic dye **2** and cationic dye **3** have the highest affinity to the branched copolymer. The absence of a relation between the nature of charged species formed by dyes **2** and **3** in water and the sorption properties of the copolymer is obviously due to the non-ionic nature of the latter. As follows from the data obtained, the zwitter-ionic structure of dye **1** in water does not favour its sorption by the branched copolymer. The electrostatic attraction forces of oppositely charged particles, apparently, prevent the sorption of dye **1**. Molecules of dyes **1**–**3** can be considered as molecular probes that allow us to assess the size of cavities where such molecules are localized. The volumes of the cavities where molecules of dyes **1**–**3** are distributed are no smaller than those of the molecules themselves and are at least hundreds of angströms.

UV-VIS, IR spectroscopy and differential scanning calorimetry were used to study the state of molecules of **1**–**3** in the polymer container and their effect on the level of intermolecular interactions in the branched copolymer–dye system. Figure 1(*a*) shows the absorption spectrum of dye **1** in the visible region. The spectrum contains a broad absorption band at 466.5 nm (curve *1*) related to π → π* transfer of hydrate form of dye **1**.[7] The shape and position of the absorption band remain almost unchanged as the concentration of dye **1** in water decreases after its immobilization by the copolymer. However, the spectrum of compound **1** immobilized in the copolymer recorded in chloroform changes considerably (curve *2*). In fact, the maximum of the absorption band shifts to shorter wavelengths ($\Delta\lambda_{\max} = 40$ nm), probably due to changing medium polarity. Dye **1** demonstrates the red shift of maximum of the absorption band with increasing solvent polarity, and the blue one at its decreasing.[8] An additional absorption appears in the spectrum at $\lambda \sim 380$ nm. This fact suggests that aggregation of charged species incorporated in the polymer occurs. It is known[9] that ionic dyes are capable of aggregation due to intermolecular interactions: $n\text{An}^- \leftrightarrow (\text{An}^-)_n$ or $n\text{Ct}^+ \leftrightarrow (\text{Ct}^+)_n$. When dispersion interactions between the π-systems of the dye molecules combined with hydrophobic interactions exceed the electrostatic repulsion of similarly charged species, stable associates are formed, dimers in a simplest case. The spectrum of a polymer film cast from $CHCl_3$ (curve *3*) maintains the shape and position of the absorption band of **1** and additional absorption is observed in the short-wave region. The absence of differences between the spectra of dye **1** incorporated in the polymer film and that incorporated in the copolymer, recorded in $CHCl_3$, suggests that the guest molecules of **1** are insulated from the environment by a polymer shell.

In the visible region, the absorption band of dye **2** in water is complex [Figure 1(*b*), curve *1*] being a superposition of two absorption bands at $\lambda_{\max} \sim 514$ and 548 nm, which correspond to the dimeric and monomeric forms,[10] respectively. The spectrum of dye **2** immobilized in the copolymer, recorded in $CHCl_3$, is transformed considerably; in particular, absorption in the visible region disappears (curve *2*). On the other hand, the spectrum of the polymer film containing dye **2** again contains an absorption band [Figure 1(*b*), curve *3*] that is a superposition of two absorption bands at $\lambda_{\max} \sim 535$ and 580 nm. It may be caused by binding of dye **2** with solvent molecules and the polymer in a complex, or the aggregation of dye **2**.

The absorption band of dye **3** in water in the visible region has two distinct maxima [Figure 1(*c*), curve *1*], which correspond to the absorption bands of the dimeric and monomeric forms of Ct$^+$ particles at $\lambda_{\max} = 613$ and 669 nm, respectively.[11] On changing the concentration of dye **3** in water from 1×10^{-4} to 0.125×10^{-4} M the D_m/D_d ratio increases from 1.2 to 1.54, *i.e.*, the dilution of the solution results in a decrease in the amount of the dimers. The spectrum of dye **3** immobilized in the copolymer, recorded

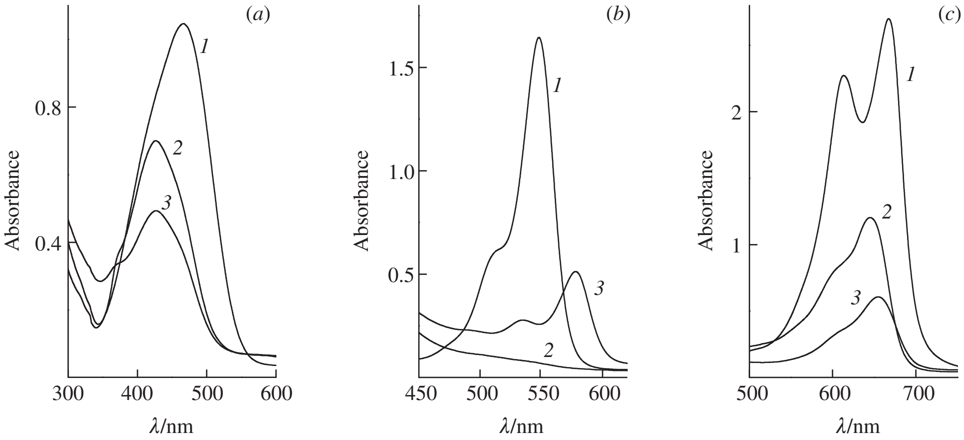

Figure 1 Absorption spectra of (*a*) dye **1**, (*b*) dye **2** and (*c*) dye **3**: (*1*) in water; (*2*) immobilized in a polymeric container in $CHCl_3$ solution and (*3*) in a polymer film cast from a $CHCl_3$ solution.

in $CHCl_3$, changes: in comparison with the aqueous solution, the absorption maxima of the monomer and dimer are shifted to shorter wavelengths of 607 and 645 nm, respectively. In this case, the monomeric form $n\mathrm{Ct}^+$ predominates over the dimeric form $(\mathrm{Ct}^+)_2$. In the spectrum of polymeric film cast from $CHCl_3$, the absorption maximum of the monomer is observed at $\lambda = 655$ nm, probably, due to a change in the polarity of the environment of Ct^+. The dimeric form decays almost completely [Figure 1(*c*), curve *3*]. Thus, transition from the aqueous solution of dye **3** to the polymeric environment suppresses the dimerization of $n\mathrm{Ct}^+$.

The IR spectra of polymer films containing dyes **1**–**3** cast from $CHCl_3$ in comparison with the original polymers remain unchanged. In some cases, the ratio of optical densities of absorption bands of C=O bonds in TEGDMA and NVP units increases, probably, as a result of interaction of the π-electrons of the C=O bond and that of aromatic rings in dyes **1**–**3**, and changing the electron density and dipole moment of the C=O bond. This allowed us to assume a non-specific (universal) character of binding of molecules **1**–**3** with macromolecules by van der Waals interactions.

Using a Mettler Toledo differential scanning calorimeter at a scanning rate of 5 K min^{-1}, we measured the T_g values of the original copolymer and copolymers containing dyes **1**–**3**. It was found that the T_g of the copolymer containing dyes **1**–**3** decreased from 81.8 to 71.4, 51.4 and 30.2 °C, respectively. Thus, dye molecules distributed inside the macromolecules of a branched copolymer affect as plasticizer and reduce the level of intermolecular interaction in the polymer chains. This increases the segmental mobility of macromolecules in a polymer nanocontainer.

In conclusion, it has been shown for the first time for hydrophilic dyes **1**–**3** as an example that branched copolymer NVP obtained by radical copolymerization in solution controlled by a chain transfer agent has high sorption properties and a sufficient excessive free volume to incapsulate hydrophilic dyes and to serve as polymeric nanocontainers.

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References

1 F. Aulenta, W. Hayes and S. Rannard, *Eur. Polym. J.*, 2003, **39**, 1741.

2 Z.-B. Zhang, Y.-H. Teng, W. Freas and D. K. Mohanty, *Macromol. Rapid Commun.*, 2006, **27**, 626.

3 N. O'Brien, A. McKee, D. C. Sherrington, A. T. Slark and A. Titterton, *Polymer*, 2000, **41**, 6027.

4 Y. Kitajyo, Y. Nawa, M. Tamaki, H. Tani, K. Takahashi, H. Kaga, T. Satoh and T. Kakuchi, *Polymer*, 2007, **48**, 4683.

5 C. Liu, C. Gao and D. Yan, *Macromolecules*, 2006, **39**, 8102.

6 P. A. Kebez, Yu. V. Leonenko, M. V. Malozemov and P. N. Nesterenko, *Vestn. Mosk. Univ., Ser. 2: Khim.*, 2006, **47**, 203 (in Russian).

7 J. Rinuy, A. Piron, P. F. Brevet, M. Blanchard-Desce and H. H. Girault, *Chem. Eur. J.*, 2000, **6**, 3434.

8 K. K. Karukstis, D. A. Savin, C. T. Loftus and N. D. D'Angelo, *J. Colloid Interface Sci.*, 1998, **203**, 157.

9 A. A. Ishchenko and S. A. Shapovalov, *Zh. Prikl. Spektrosk.*, 2004, **71**, 557 (in Russian).

10 P. Fini, M. Catucci, M. Castagnolo, P. Cosma, V. Pluchinotta and A. Agostiano, *J. Phenom. Macrocycl. Chem.*, 2007, **57**, 663.

11 S. Jockusch, N. J. Turro and D. A. Tomalia, *Macromolecules*, 1995, **28**, 7416.

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