ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 7, pp. 1274–1280. © Pleiades Publishing, Ltd., 2009.
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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Branched *N*-Vinylpyrrolidone Copolymers Suitable for Immobilization of a Water-Soluble Dye

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Received February 25, 2009

Abstract—The capability of amphiphilic branched copolymers based on *N*-vinylpyrrolidone to immobilize molecules of a water-soluble dye, Methyl Blue, by the host–guest complexation mechanism with the formation of polymeric containers was studied. The influence of the structure of the branched copolymer, agitation time, and concentration of the initial aqueous solution of Methyl Blue on the amount of the immobilized dye was examined. The behavior of dye-containing amphiphilic branched copolymers modified with alkyl methacrylates with bulky substituents in polymerizing solvents (methyl methacrylate, styrene, ethylene glycol dimethacrylate) and in the corresponding polymers was analyzed.

DOI: 10.1134/S1070427209070210

The development of highly efficient one-step procedures for preparing branched copolymers opens new prospects for designing branched copolymers based on vinyl monomers of various structures and reactivities, including *N*-vinylpyrrolidone (N-VP). Its linear (co)polymers, owing to such valuable properties as amphiphilicity and capability to sorb low-molecular-weight compounds and form with them noncovalent polymeric complexes, occupy a particular place among macromolecular compounds and are of indubitable interest for practice [4]. Unique set of properties of branched copolymers, caused by their unusual topological architecture (large amount of terminal chains in the peripheral layer), allows considerable expansion of the fields of their application, e.g., associated with immobilization of chemical compounds (catalysts, dyes, biologically active substances) inside branched macromolecules by the host–guest complexation mechanism [5–7].

The goal of this study was to examine the capability of branched copolymers based on N-VP to immobilize inside the macromolecules chemical compounds, with Methyl Blue (MB) hydrophilic dye taken as example.

EXPERIMENTAL

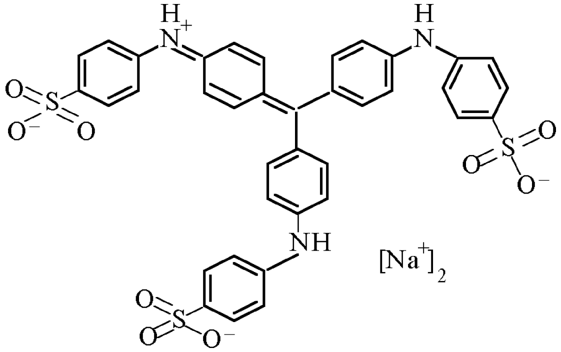
Branched N-VP copolymers of various compositions and structures were prepared by the one-step procedure [1–3] based on three-dimensional radical copolymerization of N-VP with multifunctional comonomers of various chemical structures (ethylene glycol dimethacrylate, EGDM; 1,6-hexanediol dimethacrylate, HDDM; triethylene glycol dimethacrylate, TEGDM) taken as solvents, in the presence of a chain-transfer agent, 1-decanethiol (DT). To increase excess free volume of the copolymers and enhance their diphilic properties, we introduced into the macromolecules units of alkyl methacrylates (AMAs) bearing bulky hydrocarbon (hydrophobic) substituents such as hexyl methacrylate (HMA), cyclohexyl methacrylate (c-HMA), and lauryl methacrylate (LMA).

The monomer, N-VP (Alfa Aesar), was purified to remove the inhibitor (NaOH, 0.1%) by vacuum distillation. Multifunctional comonomers EGDM, HDDM, and TEGDM, comonomers HMA, c-HMA, and LMA (Aldrich), and the solvent (ethanol) were used without additional purification. The copolymerization was performed in a three-necked flask equipped with a reflux condenser and a thermometer in an argon flow for 5.5 h at 80°C in a thermostat. The amounts of the branching agent and DT were varied in a wide range, 2 to 20 mol % relative to N-VP (0.05 mol), provided that [branching agent] $\geq$ [DT]. The concentration of the reaction mixture in ethanol was about 20 wt %. The initiator [2,2'-azobis(isobutyronitrile), AIBN] concentration was ~2×10^{-2} M. The copolymer of N-VP with methyl methacrylate (MMA), a linear analog of dimethacrylates, was synthesized in the presence of DT under the same conditions. To prepare branched copolymers modified with AMAs, we used reaction mixtures N-VP–AMA–TEGDM–DT of the composition (molar ratio) 80 : 20 : 20 : 20. The copolymers were dried in a vacuum at 60°C to constant weight. Their yield, determined gravimetrically, was 90–95%.

The rheological properties of the linear polymer and branched copolymers were studied with a VPZh-2 viscometer with a capillary diameter of 0.56 or 0.73 mm in isopropyl alcohol. By extrapolating the dependences of the reduced viscosity on the polymer concentration in isopropyl alcohol to zero concentration, we determined the intrinsic viscosity [η]. The slopes of the dependences were also determined.

The content of residual C=C bonds in branched copolymers was measured by ozonolysis using an ADS-4M double bond analyzer. To this end, solutions of the copolymers in $CHCl_3$ were prepared. Stilbene was used as a check substance.

The structural formula of MB, a water-soluble anionic dye, is given below:



A characteristic feature of ionic dyes is their capability for aggregation due to intermolecular interactions: $n\text{An}^- \leftrightarrows (\text{An}^-)_n$ or $n\text{Ct}^+ \leftrightarrows (\text{Ct}^+)_n$ [8]. When the dispersion interactions of the π systems of the dye molecules in combination with the hydrophobic interactions exceed the electrostatic repulsion of like-charged particles, stable associates (dimers in the simplest case) are formed. For example, with Methyl Blue dimerization occurs at relatively high dye concentrations (~10^{-4} M), and in the presence of anionic starlike dendrimers the dye aggregation is enhanced [9].

The branched structure of the N-VP-based copolymers and, as a consequence, the presence of excess free volume in the form of microvoids create prerequisites for immobilization of MB inside macromolecules with the formation of polymeric containers incorporating guest molecules of the dye. According to the calculations made using the Chem 3D program, the van der Waals volume of MB is about 522 Å^3. Thus, An$^-$ species can diffuse into voids in the branched copolymer whose volume is no less than the size of these species.

The fact that the copolymers on introducing methacrylate units of the branching agent and DT residues in the form of alkyl substituents $C_{10}H_{21}$ become insoluble in water allows the immobilization to be performed by joint mechanical activation of aqueous MB solutions and solutions of branched copolymers in chloroform. Incorporation of MB into the branched copolymers was performed by the following procedure: To 4 ml of a copolymer solution in chloroform (7 g l^{-1}) we added 2 ml of an aqueous MB solution $\{[\text{MB}]_0 = (0.5–4) \times 10^{-4}\text{ M}\}$. The mixture was agitated at 20°C with a shaker or a magnetic stirrer, after which it was allowed to settle to complete phase separation. The lower layer, a solution of the copolymer in chloroform, became colored. Then the upper layer, a solution of the dye in water, was removed, and its absorption spectrum in the visible range was recorded with a Specord M40 spectrophotometer. The optical density in the maximum of the MB absorption band at λ ~ 550 nm was determined, and the dependence of the optical density of the MB absorption band on its concentration in water was plotted. The linearity of this dependence indicated that the Bouguer–Lambert–Beer law was observed. This fact means that, at MB concentrations in water in the range (4–0.5) × 10^{-4} M, the dye molecules do not aggregate noticeably and occur mainly in the monomeric form. From the calibration dependence of the optical density of the MB absorption band on the MB concentration in water, we determined the MB content c_x in water. From the difference between c_0 and c_x, divided by the initial concentration of the dye in water c_0, we determined the relative amount (%) of MB incorporated in the copolymer. The experimental data were averaged over 3–6 measurements.

The branched structure of the copolymers used in this study is indirectly confirmed by the results of measuring their rheological properties in solution (Table 1). As compared to the linear polymer with $M_w \sim 30 \times 10^5$, the copolymers prepared under the same conditions and having similar MW characteristics have lower intrinsic viscosity [η] and are characterized by weak dependence of the reduced viscosity on the polymer

Table 1. Physicochemical characteristics of branched copolymers based on N-VP

(Co)polymer	Composition of N-VP–(AMA)–branching agent–DT mixture, mol %	$[\eta]$, dl g^{-1}	Slope of the dependence $\eta_{sp}c^{-1} = f(c) \times 10^2$	$[C{=}C] \times 10^3$, moles of double bonds per gram
N-VP	100:0:0	0.34	6.9	
N-VP–EGDM	100:2:2	0.23	2.9	0.2
	100:5:5	0.22	2.1	0.44
	100:8:8	0.14	2.3	0.72
	100:12:12	0.17	1.5	0.77
	100:15:15	0.08	1.4	1.11
	100:20:20	0.11	0.7	1.27
N-VP–HDDM	100:5:5	0.20	2.4	0.53
	100:12:12	0.17	1.7	0.78
	100:20:20	0.12	0.8	1.3
N-VP–TEGDM	100:5:5	0.16	1.85	0.45
	100:12:12	0.13	1.1	0.85
	100:12:10	0.082	1.9	0.62
	100:12:8	0.083	2.25	0.57
	100:12:6	0.092	2.70	0.43
	100:20:20	0.10	0.37	0.91
N-VP–HMA– TEGDM	80:(20):20:20	0.038	0.7	0.98
N-VP–c-HMA– TEGDM	80:(20):20:20	0.036	0.8	1.06
N-VP–LMA– TEGDM	80:(20):20:20	0.043	0.7	0.92

concentration in solution. These facts suggest more compact conformation (higher density of molecular packing) of their macromolecules in solution, compared to the linear analog.

The results of studying the kinetics of radical copolymerization of N-VP and EGDM in the presence of DT in ethanol by isothermal calorimetry in combination with the results of IR monitoring of separate copolymerization kinetics and with data on the composition of the branched copolymers formed [10] indicate that the copolymers in the initial steps of the polymerization are enriched in units of the more reactive comonomer, EGDM. After its complete exhaustion in the reaction mixture, the residual N-VP monomer adds to polymeric chains consisting of randomly distributed EGDM and N-VP units and undergoes homopolymerization. As a result, a copolymer with grafted chains consisting of N-VP units and linear PVP are formed. The content of linear PVP, according to gravimetric data, does not exceed 10%. The resulting copolymers are diphilic, as they consist of hydrophilic (N-VP units) and hydrophobic (methacrylate units) components differing in the thermodynamic compatibility and solubility. The diphilic structure of macromolecules of N-VP-based copolymers allows them to be considered as nonionic surfactants.

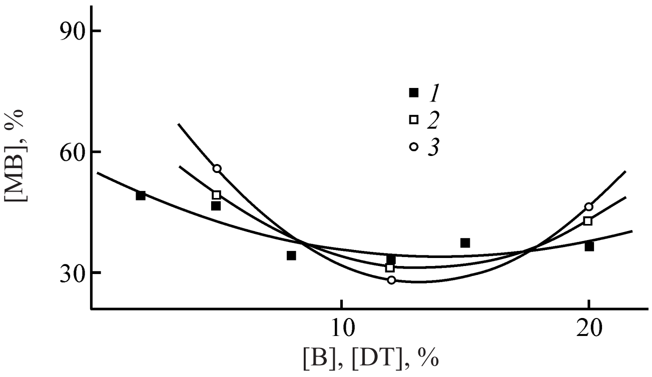


Fig. 1. Influence of the structure and composition of branched copolymers (amounts of branching agent B and DT) (*1*) N-VP–EGDM–DT, (*2*) N-VP–HDDM–DT, and (*3*) N-VP–TEGDM–DT on the amount of immobilized MB [MB]. Immobilization conditions: shaker, agitation time 10 min, initial MB concentration in water $c_0 = 2 \times 10^{-4}$ M, 20°C.

Figure 1 shows the dependences of the MB amount immobilized in the copolymers on their composition and structure. It can be seen that, under the experimental conditions (copolymer concentration in chloroform, agitation time, temperature), the copolymers take up from 30 to 60% of MB, which corresponds to (0.34–0.69) ×

10^{-2} g of MB per gram of the copolymer. The sorption capacity of the copolymer depends on the amount of the branching agent in it, passing through a minimum. The copolymers prepared with small additions of branching agents exhibit the highest sorption power. This fact seems to be quite obvious, because with an increase in the content of branching agent units the fraction of active sorption centers (N-VP units) in the copolymer macromolecules decreases. As a result, the copolymers prepared in the presence of 12 mol % branching agent and DT take up the smallest amount of MB molecules. However, further increase in the content of the branching agent in the copolymer is accompanied by an increase in its sorption power. This may be due to an increase in the excess free volume of the copolymer with an increase in the degree of its branching. As seen from Fig. 1, the chemical structure of the branching agent affects the sorption power of the copolymers insignificantly.

Of particular interest are branched copolymers prepared at the nonequimolar ratio of TEGDM (12 mol %) and DT. A decrease in the DT content in the reaction mixture leads to an increase in the degree of the copolymer branching, as indicated by the results of rheological studies (Table 1). The branched copolymers prepared at [TEGDM] > [DT] exhibited higher capability to immobilize MB. For example, the amount of MB taken up by the copolymer prepared at [TEGDM] : [DT] = 12 : 6 increases by a factor of approximately 2, compared to the copolymer prepared at the equimolar ratio of these components. This may be due to an increase in the excess free volume as a result of an increase in the degree of branching of the copolymer, leading to an increase in its sorption capacity.

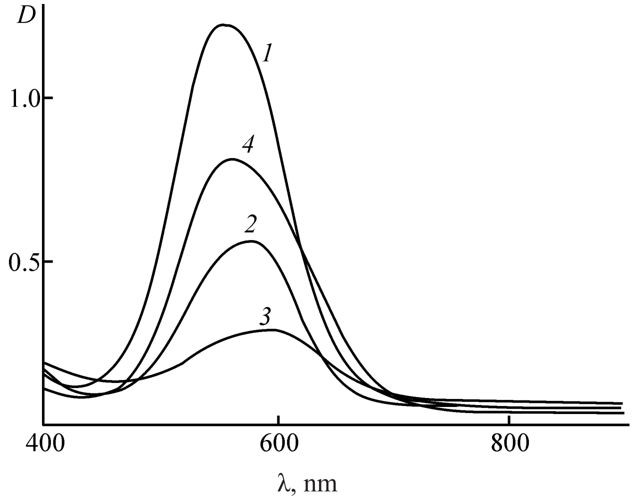


Fig. 2. Electronic spectra of MB in the visible range: (*1*) in water; (*2*) in water after immobilization of the dye with the polymer; (*3*) in a solid film of branched N-VP–TEGDM–DT copolymer cast from chloroform; and (*4*) MB immobilized in the branched copolymer, solution in chloroform. Initial MB concentration in water 2×10^{-4} M. (D) Optical density and (λ) wavelength.

The intermolecular interaction in the branched copolymer–dye system was studied by electronic and IR spectroscopy and by DSC. Figure 2 shows the visible spectra of the initial aqueous solution of MB, aqueous solution of MB after immobilization, solid copolymer film prepared from the reaction mixture N-VP–TEGDM–DT of the composition 100 : 20 : 20, and solution of the MB-containing copolymer in chloroform. At an MB concentration in water of 2×10^{-4} M, the equilibrium $n\mathrm{An}^- \leftrightarrows (\mathrm{An}^-)_n$ is shifted toward $n\mathrm{An}^-$, and MB occurs in the monomeric form, as indicated by the absorption band at $\lambda_{\max} \sim 550$ nm. Comparison of curves *1* and *2* (Fig. 2) shows that, after immobilization of a part of the dye with the polymer from water, the MB absorption maximum is shifted bathochromically to ~574 nm ($\Delta\lambda = 24$ nm), which corresponds to lower transition energy, apparently due to changes in the degree of dissociation of MB molecules or in the degree of solvation of the anions with solvent molecules. With a decrease in the MB concentration in water due to its immobilization with the polymer, the equilibrium $\mathrm{MB} \leftrightarrows \mathrm{An}^-$ is shifted toward undissociated molecules. In the polymer film, the absorption band is further shifted to $\lambda_{\max} = 588$ nm (Fig. 2, curve *3*), apparently due to replacement of the polar aqueous surrounding by the less polar polymeric surrounding. Comparison of curves *3* and *4* (Fig. 2) shows that, in chloroform, $\lambda_{\max}$ of the absorption band of MB immobilized with the polymer is shifted toward shorter wavelengths to 564 nm, apparently due to an increase in the polarity of the surrounding of MB molecules. Chloroform is a polymer solvent compatible with both hydrophobic and hydrophilic moieties of the macromolecules. Its molecules readily penetrate into polymer coils, and the polarity inside the polymeric container changes. In all the cases, as seen from Fig. 2, the MB molecules exist in the monomeric form.

The IR spectra of the branched copolymers containing MB and the initial copolymers do not differ significantly. This fact suggests nonspecific (universal) character of binding of MB molecules with the macromolecules owing to van der Waals interactions.

Incorporation of MB molecules into the branched copolymer can affect its physicochemical properties,

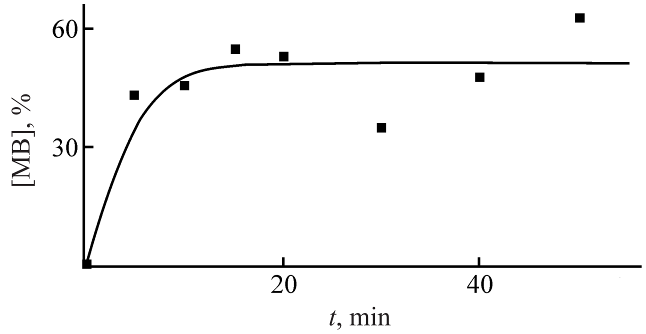


Fig. 3. Amount of MB [MB] immobilized with N-VP–TEGDM–DT copolymer prepared from the reaction mixture of the composition 100 : 20 : 20, as a function of the agitation time t. Immobilization conditions: magnetic stirrer, initial MB concentration in water $c_0 = 2 \times 10^{-4}$ M, 20°C.

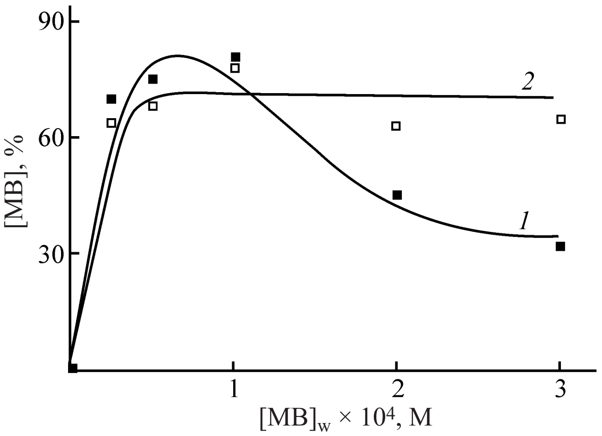


Fig. 4. Amount of MB [MB] immobilized with N-VP–TEGDM–DT copolymer prepared from the reaction mixture of the composition 100 : 20 : 20, as a function of the MB concentration in water $[MB]_w$ at an agitation time of (1) 10 and (2) 50 min. Magnetic stirrer, 20°C.

primarily those associated with the level of molecular mobility of polymer chains. This factor can be characterized, in particular, by the glass transition point T_g. Therefore, using a Mettler Toledo differential scanning calorimeter, we measured at a scanning rate of 5 deg min^{-1} the glass transition points of the initial branched copolymer prepared from the equilibrium mixture N-VP–EGDM–DT of the composition 100 : 12 : 12 and the copolymer incorporating about 1% MB. We found that T_g of the MB-containing copolymer increased by 10°C, to 102°C. This means that MV molecules distributed in the polymeric matrix affect the level of polymer–dye intermolecular interaction and decrease the segmental mobility of polymer chains.

Figure 3 shows how the amount of the dye taken up from water by the branched copolymer prepared from the reaction mixture N-VP–TEGDM–DT of the composition 100 : 20 : 20 depends on the agitation time. It can be seen that, with an increase in the agitation time, the amount of MB taken up by the copolymer from the aqueous solution increases, reaching saturation.

Figure 4 shows the isotherms of MB sorption by the copolymer prepared from the reaction mixture N-VP–TEGDM–DT of the composition 100 : 20 : 20 at two agitation times: 10 and 50 min. As can be seen, at $t = 10$ min (Fig. 4, curve *1*), the amount of MB sorbed by the polymer reaches a maximum (~80%) when its initial concentration in aqueous solution is in the range $(0.5–1) \times 10^{-4}$ M. An increase in the initial concentration of MB in water leads to a decrease in the amount of the sorbed dye by a factor of more than 2. At $t = 50$ min, the pattern is different (Fig. 4, curve *2*), and the amount of the immobilized dye is virtually independent of its initial concentration in water.

By the formula $a = (c_0 - c_x)V/m$, where V is the aqueous solution volume (l) and m is the polymer sample weight (g), we calculated the specific sorption a of MB by the copolymer prepared from the N-VP–TEGDM–DT mixture of the composition 100 : 20 : 20. We found that, in the interval of MB concentrations in water of $(0.25–3) \times 10^{-4}$ M at $t = 50$ min, this quantity is approximately 1×10^{-2} mmol g^{-1}. Close specific sorption of the patented blue dye is exhibited by super-cross-linked polystyrene (MN-200) with the particle size of 0.3–1.2 mm and specific surface area of 800–1000 m^2 g^{-1}, known as an effective sorbent of polar organic substances, including organic dyes [11]. We expected that replacement of a part of N-VP units in the branched copolymer by AMA units having bulky alkyl (hydrophobic) substituents would lead to an increase in the excess free volume of the copolymer, to a change in the hydrophobic–hydrophilic balance of the macromolecules, and to an increase in their diphilic properties. It is known that incompatibility of hydrophobic and hydrophilic blocks of macromolecules leads to intramolecular segregation even in dilute solutions: The poorly soluble block rolls up and forms the particle core, whereas the other block forms an external shell keeping the particle in solution. Such particles are capable of self-organization in solutions with the formation of various types of associates [12]. On mixing an aqueous solution of MB with a solution of the polymer in chloroform, associates of the direct micelle type, with MB molecules concentrated in the hydrophilic part, are apparently formed on the phase boundary.

Data on the amount of MB taken up by the branched copolymers N-VP–TEGDM–DT, N-VP–AMA–TEGDM–DT, and MMA–TEGDM–DT of the composition 10 : 21 : 21, and also by the linear copolymer N-VP–MMA–DT of the composition 100 : 20 : 20, are given in Table 2. It can be seen that replacement of 20 mol % of the N-VP comonomer in the copolymer composition by AMA (LMA or HMA) leads to an approximately 10% increase in the amount of the sorbed MS. Weaker effect is observed in modification of the branched copolymer with c-HMA units whose alkyl substituents, apparently, hinder sterically the sorption of MB molecules and decrease the size of voids in which bulky MB molecules can be immobilized.

Changes in the architecture of macromolecules lead to the fact that the branched copolymer N-VP–TEGDM–DT takes up a larger amount of the dye than does the linear copolymer N-VP–MMA–DT of the same composition (Table 2). This is apparently due to its branched structure and to the presence of excess free volume, i.e., of voids in macromolecules of the size sufficient for immobilization of bulky MB molecules. High capability of the branched copolymers to sorb MB molecules follows from data in Table 2 on the MMA–TEGDM–DT copolymer. Despite the absence in its branched macromolecules of active sorption centers, N-VP units, it takes up MB in a fairly large amount.

Table 2. Content of MB in branched copolymers based on N-VP. Immobilization conditions: initial concentration of MB in water 2 × 10^{-4} M, magnetic stirrer, agitation time 50 min, 20°C

Co)polymer	Composition of initial reaction mixture	MB fraction immobilized by copolymers, %
N-VP–TEGDM–DT	100:20:20	63.0
N-VP–LMA–TEGDM–DT	80:20:20:20	73.0
N-VP–LMA–TEGDM–DT	80:20:20:20	72.5
N-VP–c-HMA–TEGDM–DT	80:20:20:20	69.0
N-VP–MMA–DT	100:20:20	38.0
MMA–TEGDM–DT	100:21:21	28.5

We examined the behavior of MB-containing amphiphilic branched copolymers N-VP–AMA–TEGDM–DT, where AMA is LMA or HMA, acting of peculiar polymeric containers, in liquid media thermodynamically incompatible with separate constituents of the macromolecules. For these purposes, we took typical (di)vinyl momomers: MMA, EGDM, and styrene, in which the branched copolymers are soluble. The EGDM and styrene solutions containing 1 wt % branched copolymers N-VP–LMA(HMA)–TEGDM–DT are visually transparent and uniformly colored, whereas the solution in MMA is optically nontransparent, which suggests the formation by these copolymers of coarse associates of the inverse micelle type, with MB molecules concentrated in the hydrophilic part of the micelles. In EGDM and styrene, the copolymer is probably present in the form of monomolecular micelles, with the major fraction of MB concentrated in the core, and of small associates. The surrounding hydrophobic medium apparently prevents escape of MB molecules from the container and creates conditions for the formation of a dispersion stable in time. Despite difference in the monomer polarities, the absorption band maximum of MB occurring in the polymeric container of N-VP–LMA–TEGDM–DT in polar MMA and nonpolar styrene is observed at λ_{max} ~ 594 nm, and in EGDM it is observed at λ_{max} ~ 591 nm. The similar wavelength of the band maximum is characteristic of MB in the polymeric container of M-VP–HMA–TEGDM–DT in MMA and styrene (λ_{max} ~ 592 nm). Note that the dye molecules in a solid polymeric film of N-VP–HMA–TEGDM–DT absorb in the same region: λ_{max} ~ 591 nm. This means that the surrounding (liquid phases of different polarities or a solid polymeric matrix) exerts no significant effect on the state of MB molecules in the polymeric container, and the dye molecules are apparently isolated from the environment.

Polymerization, and especially three-dimensional radical polymerization with its characteristic phenomena, microphase segregation and microsyneresis [13], may lead to the release of MB molecules from the polymeric container and to the dye precipitation. However, actually this is not observed, and the polymers prepared by radical polymerization at 60°C and [AIBN] = 0.2 wt % of reaction mixtures of MMA, EGDM, and styrene, containing a branched copolymer of the composition N-VP–LMA(HMA)–TEGDM–DT with the immobilized MB, are uniformly colored.

The spectra of MB immobilized in branched copolymers N-VP–LMA–TEGDM–DT and in glassy PMMA show that, as compared to the liquid monomer, the absorption maximum of MB is bathochromically shifted by approximately 4 nm (λ_{max} ~ 598 nm). In the course of the polymerization, the turbidity of the reaction system, caused by addition of the polymer to MMA, considerably decreases owing to a decrease in the size and number of scattering centers. Polymerization of MMA is apparently accompanied by breakdown of the associative structure of the initial solution, with improvement of the compatibility of the formed PMMA with the introduced additive. The transmittance of the dyed PMMA at a layer thickness of 5 mm in the visible range monotonically increases and reaches 70–75%.

In the case of PS with the addition of the polymeric container VP–HMA–TEGDM–DT, the size of the scattering centers is commensurable with the visible light wavelength, and therefore the polymer becomes visually turbid. The styrene polymerization is apparently accompanied by enhanced aggregation of separate monomolecular micelles and small associates. Because of differences in the refractive indices of the dispersion medium and the dispersed phase randomly distributed in it, the final polymer becomes less transparent. The maximal transmittance of PS with 1% polymeric container with MB, at a layer thickness of 5 mm, does not exceed 45%.

The results of our studies show that branched copolymers based on N-VP exhibit high affinity for the hydrophilic dye. Their sorption capacity is determined by the structure and composition of the macromolecules and by the sorption conditions.

CONCLUSIONS

(1) As demonstrated by the example of Methyl Blue water-soluble dye, branched copolymers based on *N*-vinylpyrrolidone are capable of encapsulating foreign molecules by the mechanism of host–guest complexation with the formation of polymeric containers.

(2) The amount of the immobilized Methyl Blue is influenced by the structure of the branched copolymer, agitation time, and concentration of the initial solution of Methyl Blue in water.

(3) Methyl Blue molecules are bound to the polymer by van der Waals interactions.

(4) Methyl Blue affects the glass transition point of the branched copolymer. The segmental mobility of the polymer chains decreases in the presence of the dye.

(5) Amphiphilic branched copolymers incorporating Methyl Blue are capable of self-organization and formation of micellar associates in thermodynamically bad solvents.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 06-03-33018).

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