Synthesis and Characterization of C_{60}-Based Composites of Amphiphilic *N*-Vinylpyrrolidone/ Triethylene Glycol Dimethacrylate Copolymers

Svetlana V. Kurmaz, Nadezhda A. Obraztsova, Evgeniya O. Perepelitsina, Denis V. Anokhin, Gennadiy V. Shilov, Evgeniy N. Kabachkov, Vladimir I. Torbov, Nadezhda N. Dremova
Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka 142432, Moscow region, Russia

It was found that under mixing of aqueous solutions of copolymers and toluene solutions of C_{60} two types of polymer composites can be produced with different matrix structure, the fullerene content and an aggregation degree. The dimethacrylate enriched macromolecules migrate to toluene and the VP units enriched copolymer chains remain in water to form copolymer micelles and their aggregates in these media that solubilize and encapsulate the fullerene. The structure and properties of obtained polymer composites were studied by GPC with dual detection (RI and MALLS), FT-IR, WAXS and SAXS methods. It is shown that in a composite based on *N*-vinylpyrrolidone copolymer isolated from toluene the fullerene form larger particles, compare to that isolated from water. According to SAXS, the fullerene particles in a solid copolymer are organized in spherical objects with fine coil-like structure. The stability of the composites in water, ethanol, and chloroform was shown to depend on the original polymer matrix structure and on copolymer/fullerene ratio. POLYM. COMPOS., 35:1362–1371, 2014. © 2013 Society of Plastics Engineers

INTRODUCTION

Due to their three-dimensional structure the branched polymers show the physical and chemical properties which are different from linear analogues: higher solubility and thermodynamic compatibility with different media, low viscosity in solutions and melts, and the presence of cavities of appropriate shape and size to absorb the substances into the macromolecules to form complexes of the "host-guest" type [1, 2]. Therefore these polymers are used as adsorbents and polymeric containers to transport the various important chemicals. Change of poly-*N*-vinylpyrrolidone architecture from linear to branched and encapsulation of the fullerene or its derivatives, known for their biological activity [3, 4] opens a new perspectives of the polymer for biomedical applications.

The *N*-vinylpyrrolidone (VP)-based polymers connected with the fullerene by covalent bond [5–8] or noncovalent interactions [9–13] are well known. The efficiency of the fullerene as functional agent is suggested to be [11] higher in case of noncovalent bonding when electronic structure is subjected to minimum change. Such VP polymer/fullerene complexes in which C_{60} (π-acceptor) is bonded to the polymer chain by donor-acceptor interactions (a charge transfer complex) are produced by separation from a solution of the VP-based polymer and fullerene in an organic solvent or by solid-phase interaction and extraction by water [9–13]. Noncovalent binding between the water-soluble polymer and fullerene provide its better solubility. Structure and properties of these complexes in water is often the subject of special studies [14]. As the result, aqueous solutions PVP/C_{60} are proposed to use as biological tests (hemolysis test) [15]. According to [16], PVP/C_{60} complexes exhibit virocidal activity: they act mainly on the lipid component of virus membranes.

The problem is that the fullerene is difficult to disperse in the polymer matrix due to its tendency to aggregate and form crystallites. The synthetic methods have been developed to prepare the polymer composites in form of stable colloidal dispersions by polymerization in an aqueous-organic emulsion containing fullerene. So, PS/C_{60} nanoparticles were obtained by emulsion polymerization of styrene in the presence of water in poly-*N*-vinyl pyridine as stabilizer [17]. The pristine C_{60} was homogeneously distributed in the polymer matrix. Polyaniline/C_{60} composites were prepared by polymerization of aniline hydrochloride in water-benzene emulsion containing fullerene [18].

Currently, the supramolecular chemistry approach is actively used to produce the composites with a controlled structure and properties by the control of the fullerene

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Correspondence to: Svetlana V. Kurmaz; e-mail: skurmaz@icp.ac.ru

Contract grant sponsor: Russian Foundation for Basic Research (to D.V.A.); contract grant number: 12-03-31654.
DOI 10.1002/pc.22788

aggregation process. In this case, the spontaneous aggregation of the polymer colloid and C_{60} in an organic solvent leads to the formation of stable colloid polymer-fullerene particles. The amphiphilic block copolymers are suitable for this purpose because they are able to self-organize in a media which is a good solvent for one block and precipitator for another block [19]. Block copolymers bearing of linear and dendritic fragments in special solvents (THF/water) can aggregate in form of spherical micelles as well [20]. For example, polymer composites were obtained by mixing a solution of the polymer colloid based on amphiphilic block copolymers (emulsions and micelles) and C_{60} in toluene solution with following separation from the solution [4, 21–25]. As the result, C_{60} was converted in water-soluble colloid state and can be used in biomedical applications as photosensitizers for photodynamic cancer therapy [4].

On mixing of micellar solutions of PS/poly-*N*,*N*-dimethylaminoethyl methacrylate (PS-PDMAEMA) amphiphilic block copolymers with a toluene solution of fullerene, the latter interacts with a micellar particle resulting in self-assembly of the fullerene into clusters of different sizes [21]. Moreover, polymers containing electron-donor atoms (oxygen, nitrogen) are able to associate in charge-transfer complexes with the fullerene [21, 25]. The results of the comparative study on the aggregation of the fullerene with the block copolymer PS-PDMAEMA and polar PDMAEMA homopolymer [21] show that the interaction of the micellar particles with fullerene to be a rapid process. In this case, the fullerene is deposited on the surface of the PS-micellar core to organize stable colloidal particles. In contrast, two competing processes, the interaction of the fullerene with the polar shell micellar particles [21] and the formation of charge-transfer complexes, e.g., between C_{60} and a block-copolymer of PS-P4VP [25] are characterized by low rate.

In this article, the branched VP copolymers colloids in water were used to fabricate the C_{60}/copolymer composite for the first time. The choose of polymer objects are determined, first of all, by their ability to aggregate in water due to diphilic nature, the macromolecule size and biocompatibility. As is known, the polymers for medical applications have strict limits in their molecular weight, as it affects on the excretion rate. Usually, the polymers with molecular weight $\sim 10^4$ are applicable for these purposes. The linear and branched (co)polymers of VP synthesized by radical polymerization in solution respond to these conditions. Radical copolymerization of vinyl monomers with bifunctional comonomers in the presence of thiols as chain transfer agent is facile one-pot method to prepare the branched copolymers of desired topology [26–31].

In the present article, the preparation and characterization of polymer composites based on amphiphilic copolymers of *N*-vinylpyrrolidone with triethylene glycol dimethacrylate from toluene-water mixtures is described.

EXPERIMENTAL

Materials

The copolymers of VP and triethylene glycol dimethacrylate (TEGDM) obtained by radical copolymerization in toluene with and without of 1-decanethiol (DT) by the method described in Ref. 32 were used. At the molar ratio [VP]:[TEGDM]:[DT] 100:5:0, 100:5:5, 100:12:12, the B0, B5, and B12 (the number in the notation of (co)polymer corresponds to the DT amount in the reaction mixture VP-TEGDM-DT) copolymers were obtained, respectively. Similarly, at a molar ratio [VP]:[DT] 100:1 and 100:3 the linear L1 and L3 polymers were yielded.

As-received fullerene C_{60} ($\sim$99.95% purity, JSC "Fullerene-Center," Nizhny Novgorod, Russia) was used in the experiments.

The Synthesis of Copolymer Composite from Water-Toluene Mixture

The 7 mg/ml solutions of copolymers were prepared in distilled water, and the fullerene was dissolved in freshly distilled toluene (0.7 mg/ml). The solubility of C_{60} at room temperature is about 2.9 mg/ml [33]. It is believed that the fullerene in solution is in the form of clusters consisting of several molecules, the average cluster size decreases slowly as the concentration of the solution is reduced. With a substantial dilution of the solution (to three orders of magnitude lower saturated value) the clusters were not identified and only isolated fullerene molecule present in the solution. Here, fullerene in toluene, apparently, exists in the form of clusters of different sizes.

Later, the aqueous solutions of VP copolymers and toluene solutions of fullerene were mixed at various volume ratios: 1:1, 1:2, and 2:1. In this case, the mixtures contained 280, 280, and 140 mg copolymer, and 28, 14, and 28 mg of C_{60}, respectively. The mixture was stirred for 1 h with a magnetic stirrer at room temperature. A rapidly separated emulsion is formed at stirring of water and toluene. However, in the presence of polymer additives its stability increases, apparently due to the stabilizing effect of copolymers as non-ionic surfactants.

The coalescence of droplets of the dispersion phase leads to the destruction of the emulsion into two phases, which were separated on the funnel. The toluene phase, being visually clear or cloudy, possesses a purple color typical for fullerene solutions in aromatic solvent. The aqueous phase was characterized by different degrees of turbidity as well.

The solvents were removed by drying of polymer composites in air and in vacuum. Finally, powders of polymer composites of different colors were produced. Products isolated from toluene and aqueous solutions have dark brown and yellow-brown color, respectively.

In the same manner the fullerene was encapsulated in linear L1 and L3 homopolymers.

Instrumentation

Dynamic Light Scattering. The hydrodynamic radius R_h of the polymer particles in water was determined by DLS (Photocor FC, $\lambda = 690$ nm) at 20°C. The concentration of the aqueous solutions of L1, L3, B0, B5, and B12 was 0.7 wt%. Before measuring the solutions were filtered using a filter with a pore diameter 0.45 μm. The experimental data were performed by the software Dynals v2.0.

Gel Permeation Chromatography with Dual Detectors (RI and MALLS). Molecular weight of (co)polymers and some polymer composites were measured by GPC using HPLC Waters GPCV 2000 (two columns PL-gel, 5 microns, MIXED-C, 300 × 7.5 mm) equipped by refractometric detector (RI) and light scattering detector WYATT DAWN HELEOS II ($\lambda = 658$ nm) (MALLS). Absolute molecular weights of the copolymers were determined from data of RI and MALLS detectors. Software Astra, version 5.3.2.20, was used. *N*-methylpyrrolidone with 1 wt% of LiCl was used as eluent to suppress an aggregation of (co)polymer. The elution rate was 1 ml/min, $T = 70$°C, the refractive increment dn/dc ~0.06 to 0.07 ml/g.

FT-IR and UV-Vis Absorption Spectroscopy. The copolymer composition was determined by IR spectroscopy via dependences of the optical density D of the absorption band at 1674 cm^{-1} related to the stretching vibrations of the C=O bond in lactam ring of VP on the concentration of copolymers in chloroform. The VP units content in the copolymers was estimated using the calibration curve for linear homopolymer. IR spectra of the initial (co)polymers and composites were recorded on a FTIR Bruker ALPHA spectrometer at 16 scans per spectrum in the 4000 to 400 cm^{-1}. Films of samples were deposited on KBr glasses from chloroform and air-dried. UV-Vis absorption spectra of solutions of polymer composites were recorded with a spectrophotometer Specord M40. The cell thickness was 0.5 or 1 cm.

Optical Microscopy of Polymer Composite Films and Scanning Electron Microscopy of Polymer Composite Powders. The morphology of polymer composite films was studied using optical microscope Zeiss Axio Imager A1 (Germany) in transmitted light (dark field). The films were cast by pouring on glass slides using 0.5% solutions of the composites in chloroform, and kept on air to evaporate $CHCl_3$. The electron microscopy images of the carbon-coated copolymer composites were obtained by emission scanning electron microscope Zeiss LEO SUPRA 25.

X-ray Scattering (WAXS and SAXS) of Polymer Composite. X-ray scattering experiments (WAXS) of powders were performed on diffractometer ARLX'TRA (Thermo electrocorporation) with copper radiation at 25°C. The small-angle X-ray scattering (SAXS) study of polymer composite film were carried out using a diffractometer Xenocs with a generator GeniX3D ($\lambda = 1.54$Å), that is forming a beam of 300 × 300 μm size. Two-dimensional diffractograms were recorded using a detector Pilatus 300k with sample-to-detector distance of 2.5 m. Modulus of the wave vector s ($s = 2\sin\theta/\lambda$, where θ is a Bragg angle) was calibrated using the seven diffraction orders from a sample of rat tail collagen.

RESULTS AND DISCUSSION

The VP-TEGDM Copolymers Characterization

The VP-TEGDM copolymers obtained at various reaction mixtures differ by composition, the topological structure, physico-chemical parameters and diphilic nature. According to IR-spectroscopy data, the B0 and B5 copolymers contain ~0.82 and 0.18 mole fractions of VP and TEGDM units, respectively. The B12 copolymer consists of 0.67 and 0.33 mole fractions of VP and dimethacrylate units, respectively. The experimental composition are in good agreement with calculations by the equation of the copolymer composition and the values of relative reactivity of comonomers $r_{VP} = 0.16$ and $r_{MMA} = 1.30$ (MMA is linear analog of TEGDM) [34].

The comonomer TEGDM acts as a branching agent because of double bonds in the side chains involved in the polymer chains growth. Their topological structure (the length of the primary and cross-site polymer chains, the number of branches) depends on the ratio [VP]:[TEGDM]:[DT], the propagation rate constant k_p and the chain transfer constant k_{tr} to the DT [32]. With increasing of branching agent content the length of cross-site chains decreases, and a number of branches grows. Equimolar [TEGDM]:[DT] ratio allows to completely suppress the cross-linking reactions resulting in the formation of network copolymers.

These copolymers are different from linear PVP by the absolute values of molecular weight, polydispersity and the glass transition temperature (Table 1).

Figure 1 shows the curves of MWD for linear L1, L3 homopolymers, and the B0, B5, and B12 copolymers as well as the dependencies of the absolute values of average molecular weight M_w on the retention volume V_R. On can see that the MWD curves of copolymers are polymodal with a shifts to lower molecular weights compared to linear polymers. With the increasing of the DT content in the reaction mixture the portion of high molecular weight copolymer decreases (see the curves for B0 and B5). With increasing of the TEGDM content in copolymer and, accordingly, DT the portion of low-molecular weight

TABLE 1. Physicochemical characteristics of VP (co)polymers.

(Co)polymer	The reaction mixture composition [VP]:[TEGDM]:[DT]	$M_w \times 10^{-3}$	PD	T_g (°C)
L1	100:0:1	49.8	2.8	139
L3	100:0:3	43.4	2.6	125
B0	100:5:0	47.2	5.5	72.0
B5	100:5:5	23.6	2.6	75.6
B12	100:12:12	21.1	3.6	63.3

component grows (to compare the curves for the B5 and B12). The reason is the reaction of chain transfer [32], which restricts the growth of polymer chains

$$R_n^{\bullet} + RSH \rightarrow R_nH + RS^{\bullet}$$
$$RS^{\bullet} + M \rightarrow RSR_n^{\bullet}$$

The results of chemical analysis [35] indicate the presence of sulfur in the VP-TEGDM copolymers, i.e., $-SC_{10}H_{21}$ groups are incorporated into the copolymer chain owing to chain transfer reaction. Approximately 70% of DT added to the reaction mixture, involved in the chain transfer reaction. As a consequence, the molecular weight of the copolymers is decreased (Table 1). These copolymers are characterized by lower values of the glass transition temperature T_g compare to homopolymers. It decreases further with end chains number increase for the B12 copolymer.

Inclusion of TEGDM units and DT residues in polar polymer chain consisting of VP units leads to increase the concentration of moieties of diphilic nature and ability to form aggregates of different sizes in water. However, linear VP polymers self-assemble in aqueous solutions as well. This is supported by visual analysis of L1 and L3 aqueous solutions and their electron absorption spectroscopy data (Fig. 2). Thus, 1 wt% solution of L1 polymer in water is optically transparent, and 5 wt% solution is a slightly opalescent. The hydrophobic nature of polymers is enhanced as the DT content in polymer chains increases, and as a result, already 1 wt% aqueous solution of L3 polymer becomes opalescent. As the concentration of L3 polymer in water grows, the transparency of solutions decreased and, consequently, the optical density of solutions increases in the visible region (Fig. 2a). In the studied concentration range, the macromolecules of L3 are presented in the form of aggregates of micellar type. The appearance of aggregates of this kind in water has been established experimentally by fluorescence spectroscopy of other water-soluble polymers, such as acrylamide polymers containing very small additions of hydrophobically modified moieties [36].

Moreover, according to the MALLS data, the effective absolute M_w values of L3 homopolymer can reach 10^6 to 10^7 (Fig. 1b) that is in the bad agreement with the conditions of its synthesis because with increasing of DT content in the reaction mixture one can expected a decrease of the molecular weight of the polymer due to a chain transfer reaction. The reason can be the appearance of large L3 polymer aggregates in N-methylpyrrolidone as a polar eluent. The sign for this is the higher content of hydrophobic residues of DT in the polymer chains than that in L1.

Aqueous solutions of B0 and B5 copolymers are almost transparent in the visible region (Fig. 2b, curves *3*, *4*). However, an aqueous solution of the same concentration of B12 copolymer is less transparent. Probably, its macromolecules form aggregates whose size is comparable with the wavelength of visible light. As a consequence, light scattering is observed on colloidal particles (Fig. 2b, curve 5).

According to DLS, L1, L3, B0, B5, and B12 (co)polymer particles have different size in aqueous solutions. The particle size distribution is bimodal for L1 polymer:

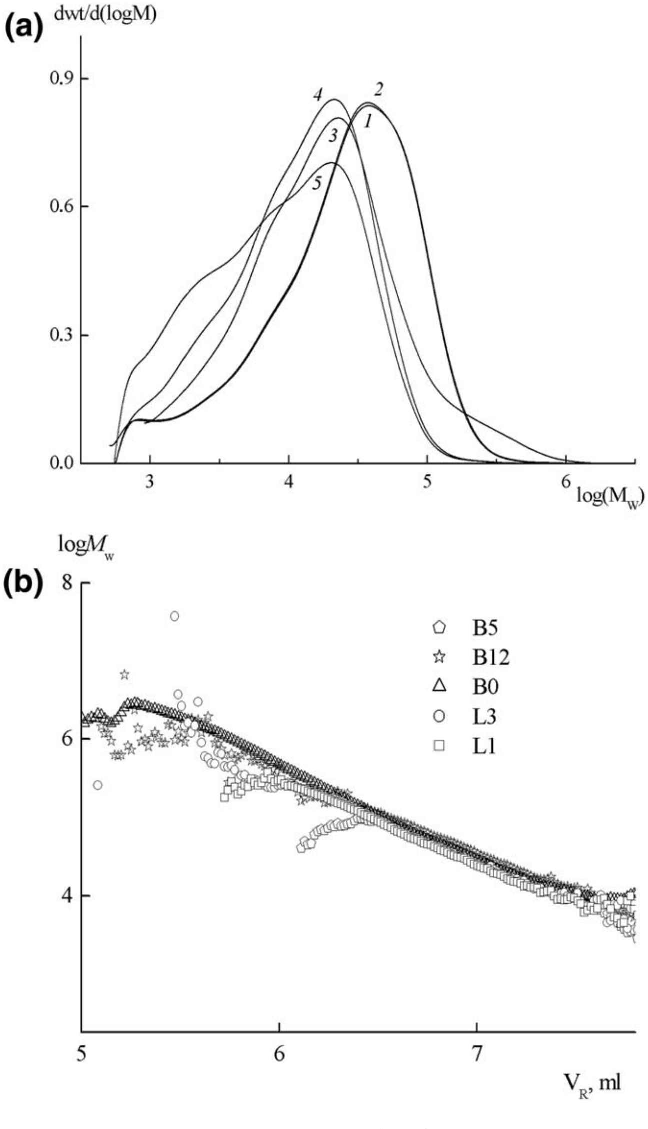

FIG. 1. MWD curves (a) and dependencies of Mw absolute values on retention volume V_R (b) for L1 (1), L3 (2), B0 (3), B5 (4), and B12 (5) (co)polymers.

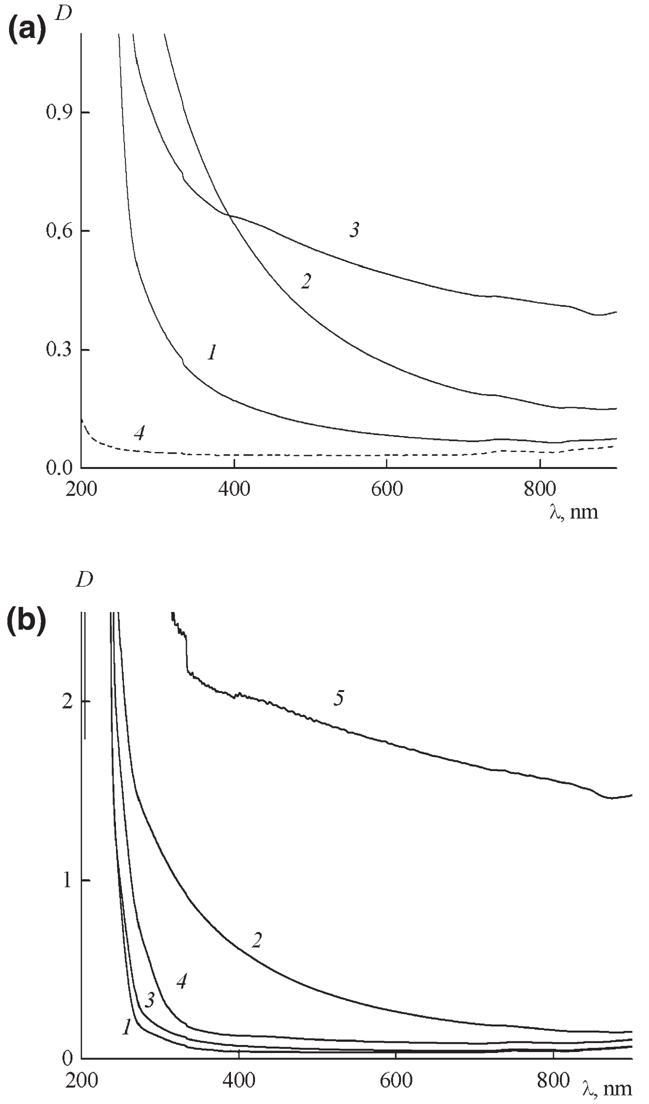

FIG. 2. (a) UV spectra of 0.5 (1), 0.75 (2) 1.0 (3) wt% aqueous solutions of L3 polymer and water (4); (b) UV spectra of the 0.7 wt% solutions of L1 (1), L3 (2), B0 (3), B5 (4), and B12 (5) (co)polymers. The cell thickness is 1 cm.

the average hydrodynamic radii of polymer particles are ~4 and ~34 nm. For L3 polymer along with particles of the same size (~4 and ~25 nm) the particles of significantly larger size (~200 nm) appear. For B0 copolymer average particle sizes increase to ~5 and ~52 nm, respectively. As in the case of L3 polymer, the B5 copolymer is characterized by broader range of particles (~3, ~56, and ~200 nm). For B12 copolymer the majority of particles have size of ~130 nm.

Special experiments showed that the TEGDM enriched macromolecules tend to migrate to toluene under mixing of the B0 aqueous solution and toluene. Meanwhile, the hydrophilic macromolecules remain in water. A certain portion of toluene is occurred in the water as solubilizate. It is known [37] that the aqueous micellar solutions of non-ionic surfactants solubilize toluene. The absorption spectroscopy indicates the presence of toluene in aqueous solutions of (co)polymers after phase separation. We observed absorbance in the UV-spectra at 260 to 280 nm, typical for toluene.

The TEGDM enriched macromolecules isolated from water form aggregates of various sizes; the hydrodynamic radius of the particles was 3, 13, and 96 nm. Meanwhile, the particle sizes formed by more hydrophilic macromolecules, were about 5 and 41 nm. R_h values for the all investigated copolymer may correspond to three types of particles: single macromolecules, micelles and their aggregates—intermicellar clusters [38]. The hydrophilic macromolecules of the B0 copolymer form small particles with more narrow size distribution in water.

The Copolymer Composite Characterization

From preliminary experiments, it was shown that the polymer particles of different sizes formed by macromolecules with various diphilic nature present in water and toluene after mixing of water-toluene solutions. Obviously, such a separation of copolymers on hydrophilic and hydrophobic macromolecules occurs under encapsulation of C_{60} from water-toluene mixtures. Nonpolar toluene with dissolved hydrophobic fullerene solubilized by methacrylate core of copolymer micelles and intermicellar clusters of aqueous phase. As a result, the fullerene is encapsulated in hydrophilic macromolecules of VP-TEGDM copolymers. Probably, some part of the copolymer chains can adsorb at the interface of C_{60}. Solid powders of polymer composites based on hydrophilic macromolecules are produced after removing of organic solvent. More hydrophobic macromolecule of copolymers migrated in toluene, apparently, also self-assembled to form a micelle structure with polar core and to solubilizate the fullerene. Owing to solubilization and encapsulation of C_{60} by copolymers, the macromolecular complexes of "host-guest" type are formed. If the fullerene known as an electron acceptor and hydrophilic donor converge at less than 5–6 Å [39], one can expect the formation of a charge-transfer complex. The encapsulation and drying composites from water and toluene is accompanied by aggregation of the fullerene to form the clusters of different sizes dispersed in a polymeric matrix.

According to FT-IR, the polymer matrix of the polymer composites based on B0, B5 and B12 copolymers separated from water and toluene differ by molecular structure. The intensity of stretching vibrations of C=O bond in methacrylate group at 1721 cm^{-1} is significantly lower in the IR spectra of composites (Fig. 3), isolated from water, than that of the composites isolated from toluene. This shows that macromolecule with low and high concentration of methacrylate groups present in water and toluene, respectively. As a result, structure and composition of the polymer matrix in composites, isolated from water and toluene, is different. In the first case, the copolymer consists of VP-units mainly. In the second case, the polymer matrix is a copolymer with high content of

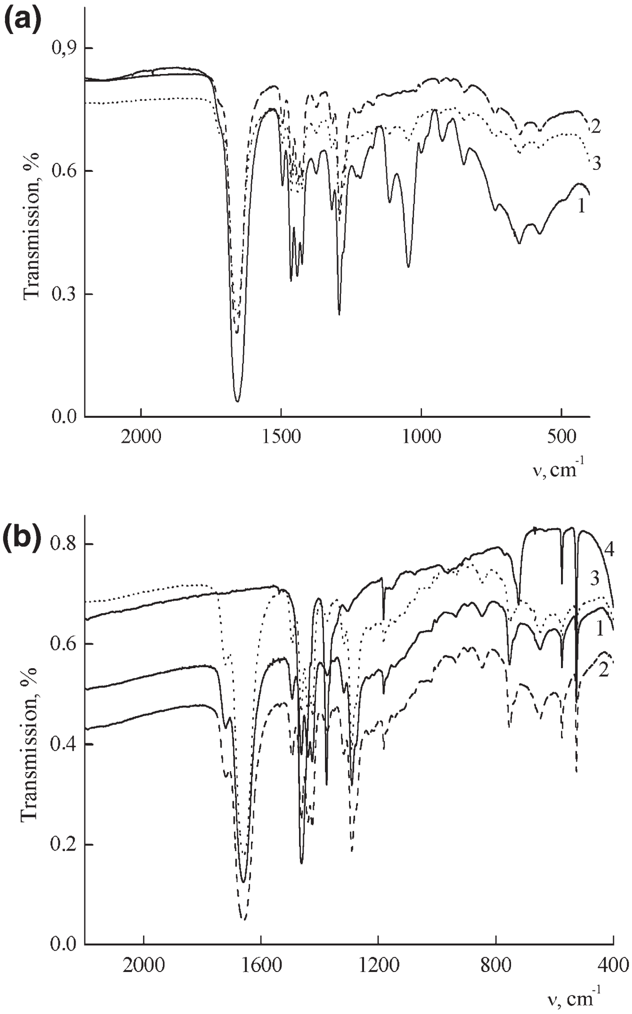

FIG. 3. IR spectra of polymer composites obtained at various volume ratios of aqueous solution of the B0 copolymer and toluene solution of the fullerene: 1:1 (1), 1:2 (2), and 2:1 (3). a, b correspond to the IR spectra of composites, isolated from water and toluene, respectively. To compare the IR spectrum of fullerene (4) in mineral oil is given.

methacrylate groups and, therefore, with large amount of branches.

The molecular-weight characteristics analysis of the initial B0 copolymer and polymer composites (Table 2) indicates that the macromolecules with higher molecular weight are presented in water rather than in toluene. According to gravimetric data, from 50 to 80% of the B0 copolymer remains in water depending on volume ratios of mixing solutions.

Figure 4 shows micrographs of B0/C_{60} composites isolated from toluene and water. The former is characterized by large aggregates of the copolymer particles separated by channels. Consequently, it has a porous structure with developed specific surface area. The latter is, in contrast, characterized by dense surface formed by small particles (about 20 nm). Apparently, strong intermolecular interactions of polymer chains enriched by VP-units results in good engagement of the copolymer particles.

The presence of fullerene in polymer products is confirmed by absorption spectroscopy, FT-IR, WAXS, SAXS, and optical microscopy. The absorption IR spectra with intense bands at 576 and 527 cm^{-1} indicate that the isolated from toluene composites at any copolymer:C_{60} ratio contain large amount of the fullerene (Fig. 3b). Particularly, according to gravimetric data, the fullerene content in the B5-based composite isolated from toluene was 45 (1:1), 35 (1:2), and 25% (2:1). However, the characteristic absorption bands of the fullerene do not observed in the IR spectra of composites, isolated from water. We compared the IR spectra of the initial fullerene and composites, isolated from toluene (Fig. 3b). The characteristic frequencies of the absorption bands at 576 and 527 cm^{-1} of the original fullerene do not change in the IR spectra of the composites. Probably, these polymer products contain the native fullerene and the later forms a complex of the "host-guest" type with the copolymer.

Figure 5 shows the powder diffractograms of the B0-based composites, isolated from toluene and water, as well as of the B0 copolymer. In addition to polymer amorphous halo the narrow peaks of fullerene crystalline phase can be identified (Fig. 5a).The analysis of positions and intensity of the peaks in the range 10 to 35° reveals the formation of cubic phase of C_{60}.

The diffractograms of composites isolated from water (Fig. 5b) show the broad overlapping peaks, which correspond to the formation of small imperfect crystals of fullerene in the amorphous matrix of B0. The presence of C_{60} in the polymer composite is confirmed by absorption spectra of these composites in chloroform. Perhaps, the degree of crystallinity of the fullerene in the composite is low or the C_{60} molecules are molecularly dispersed in B0 copolymer at encapsulation. Thus, these two types of composites are different not only by the content of the fullerene but by content and size of crystal phase. In composites isolated from toluene the fullerene contained in the form of crystallites of large size weekly interacting with the polymer chains.

One-dimensional spectra obtained by integrating of two-dimensional diffractograms of polymer composites isolated from water demonstrate no peaks. It indicates the

TABLE 2. MW-characteristics of B0 copolymers containing in B0/C_{60} composite (RI).

The composite based on B0 copolymer isolated from	Volume ratios of aqueous solution of B0 copolymer and toluene solution of C_{60}	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	PD	$M_p \times 10^{-3}$
Water	1:1	8.4	35.1	4.2	23.3
	1:2	9.7	39.6	4.1	23.5
	2:1	8.1	33.2	4.1	22.7
Toluene	1:1	2.2	15.8	7.1	2.0
	1:2	2.1	10.8	5.1	1.9
	2:1	2.4	20.2	8.4	2.2

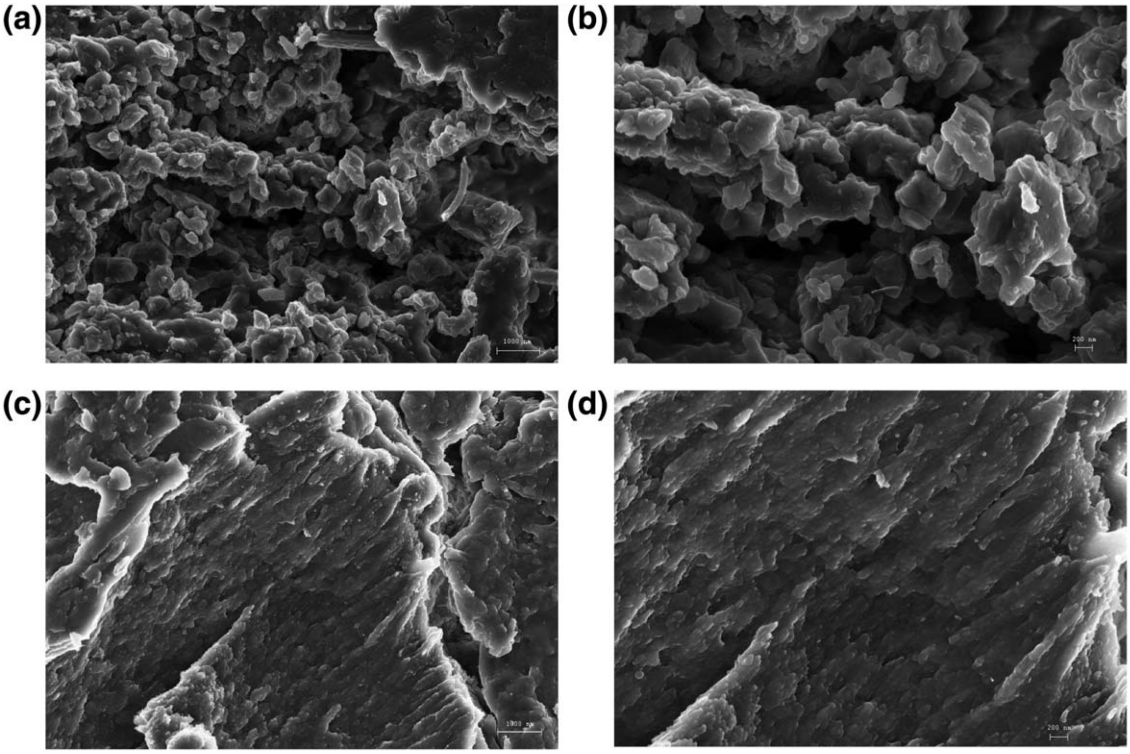

FIG. 4. Surface microphotographs of the composite powders of B0/C_{60} isolated from toluene (a, b) and water (c, d). The volume ratio of aqueous solution of B0 copolymer and C_{60} in toluene is 1:2.

absence of regular crystal stacks in polymer matrix. The curve in logarithmic coordinates shows two linear sections (Fig. 6). The mass fractal dimension of system d_m was calculated from the slope of the curve. In the s range of 0.001 to 0.005 Å^{-1} d_m is equal to 2.9; it corresponds to dense spherical aggregates. Whereas, in the s range of 0.007 to 0.022 Å^{-1} the mass fractal dimension d_m is equal to 1.2 that is typical for a thread-like structure. Thus, the C_{60} particles are coil-like structures of complex geometry.

Microphotograph (Fig. 7) shows the structure of C_{60} in the B5-based composite isolated from water on larger scale. The average size of spherical aggregates in ordered chain-like structures is about 10 microns.

The fullerene was also encapsulated in L1 and L3 homopolymers, which differ in content of -$SC_{10}H_{21}$ groups in polymer chains and the ability to aggregate in water. According to gravimetric data, over 90% of L1 and L3 polymer remains in water. Polymer composites based on L1, isolated from water, have a bright cream color, while L3-based composites were colored more intensively. Obviously, L3 homopolymer encapsulates more C_{60} compared with L1 in these experiments.

The amount of the fullerene in polymer composites based on L1, L3, B0, B5, and B12, isolated from water, was evaluated by UV-Vis absorption spectroscopy. UV spectra of polymer composites were recorded for this in chloroform (Fig. 8), where the polymer-C_{60} complex dissociates. As a result, characteristic absorption bands of the fullerene molecules releases in $CHCl_3$ can be detected in the UV spectra. Based on the intensities of the fullerene absorption bands at 260 and 330 nm one can conclude that the highest amount of C_{60} is contained in composites based on B5 and B12 copolymers. It is also was detected in the composite based on L3 with two to three times less content compared with copolymers mentioned above. Further decrease of fullerene content was revealed for the composite based on L1. Thus, VP copolymers are more efficient in fullerene encapsulation from water−toluene mixture than VP homopolymers. The B5 and B12 copolymers formed a large aggregates in water can encapsulate more fullerene than other copolymers.

Figure 8 also shows the spectrum of the fullerene in chloroform (3.2×10^{-5} M) that allows estimating the amount of C_{60} in the composites solution in chloroform from the intensity of absorption band at 330 nm. In the solution of composite based on B5 the amount of the fullerene is appeared to be three times less than of the free fullerene in chloroform. After the recalculation on mass of copolymer the content of C_{60} in the composite was found about 0.15 wt%. For other composites the fullerene content was found to be less.

Solubility and Stability of Polymer Composites in Various Media

For biomedical applications it is very important to make polymer composites soluble in water and similar

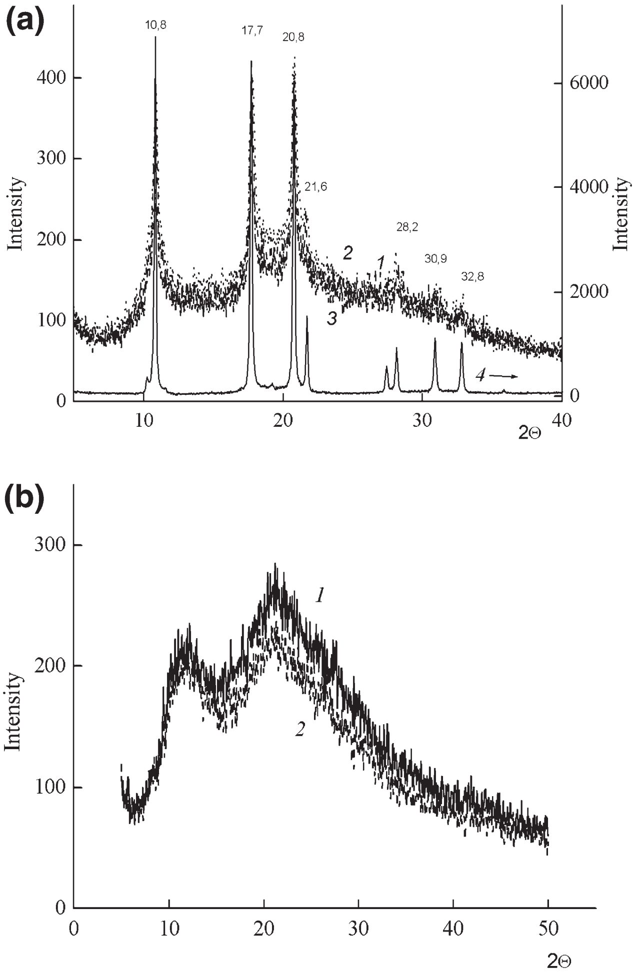

FIG. 5. Diffractograms of B0-based polymer composites obtained at different volume ratios of aqueous solution of the copolymer and toluene solution of C_{60}: 1:1 (1), 1:2 (2), and 2:1 (3) and C_{60} powder (4); the composites were isolated from toluene (a). The diffractograms of the B0 copolymer (1) and the copolymer composites isolated from water, 1:2 (2) (b). The numbers at peaks on diffractograms correspond to the diffraction angle 2θ.

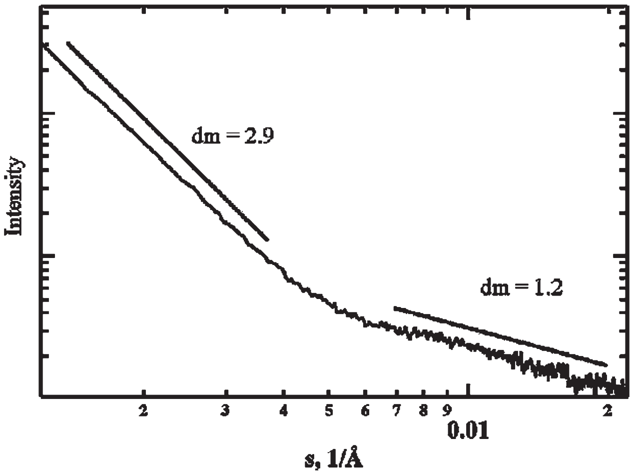

FIG. 6. The diffractogram of the B0/C_{60} composite, isolated from water. The volume ratio of aqueous solution of the copolymer and a fullerene solution in toluene is 2:1.

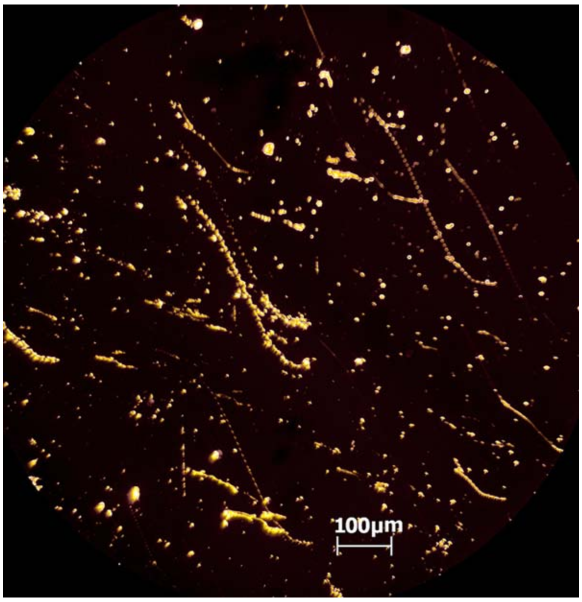

FIG. 7. The optical microphotograph of the composite based on B5 copolymer (2:1) isolated from water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

media (alcohols, etc.) with stable colloid solutions. Therein, the solubility of B0/C_{60} (1:2, 2:1), B5/C_{60} (1:1, 2:1), and B12/C_{60} (1:1) composites isolated from water and toluene have been examined in water and ethanol, which are precipitators of fullerene in the respect to their solubility in chloroform that is a good solvent of the copolymers. The electronic structure of fullerene in these media was addressed by UV spectra of composite solutions.

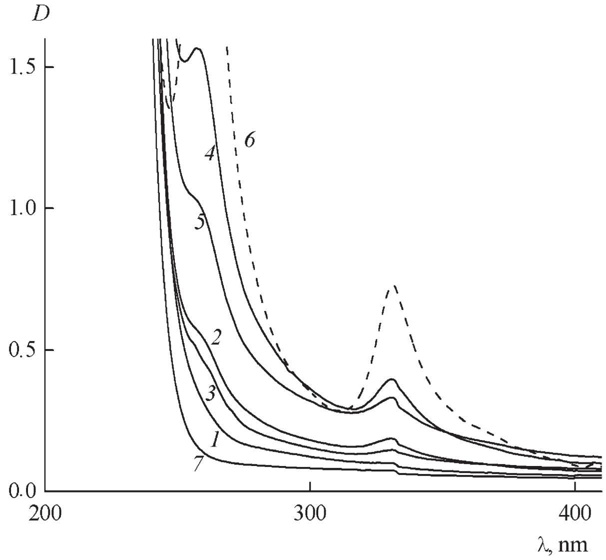

FIG. 8. UV spectra of the (co)polymer composites isolated from water produced at 1:1 volume ratio of aqueous solution of L1 (1), L3 (2), B0 (3), B5 (4), B 12 (5) (co)polymers and fullerene solution in toluene and the fullerene in chloroform (6) and chloroform (7). 10 mg of (co)polymer composite was dissolved in 2 ml of chloroform. The cell thickness is 0.5 cm.

B0/C_{60} composites, isolated from water, are completely soluble in water, ethanol and chloroform, and their 1 wt% solutions are visually transparent and stable; the fullerene particles do not precipitate from the solutions under storing. In all cases, UV spectra of aqueous solutions of composites (Fig. 9) contain the absorption attributed to the inclusion complex [40]. Apparently, the fullerene is kept in water by hydrophobic and donor-acceptor interactions with polymer chains [11].

Stable water and ethanol solutions of B5/C_{60} composites (1:1) isolated from water have a yellowish color, whereas the solution in chloroform was colorless. However, the aqueous solution of the same composite but obtained at ratio 2:1 was less stable: the C_{60} particles separated from it over time.

The composites, selected from toluene, are significantly different by solubility and stability in the same media. Their 1 wt% solutions in water, ethanol and chloroform were colored in brown, and the composite showed low stability in these solvents: the C_{60} particles precipitated at the bottom of the vials. Such instability can be explained by weak interaction of the large fullerene crystallites with the polymer matrix.

The composites based on B12 (1:1), isolated from water, are also dissolved completely resulting in formation of clear yellowish solution in ethanol and chloroform. In addition to a yellowish color, the aqueous solution is slightly opalescent revealing that in the solution B12/C_{60} composite exist in the form of multimolecular associates of large size.

Figure 10a shows the UV spectra of 1 wt% solutions of B5/C_{60} composite in ethanol and chloroform. In the spectrum of the composite in chloroform the absorption band of free fullerene appears at 330 nm. The same effect was found for a solution of composite based on B12 in chloroform (Fig. 10b, curve *1*). However, this band does not present in other solvents. The spectrum of the encapsulated in polymers fullerene is changed both in water and in ethanol.

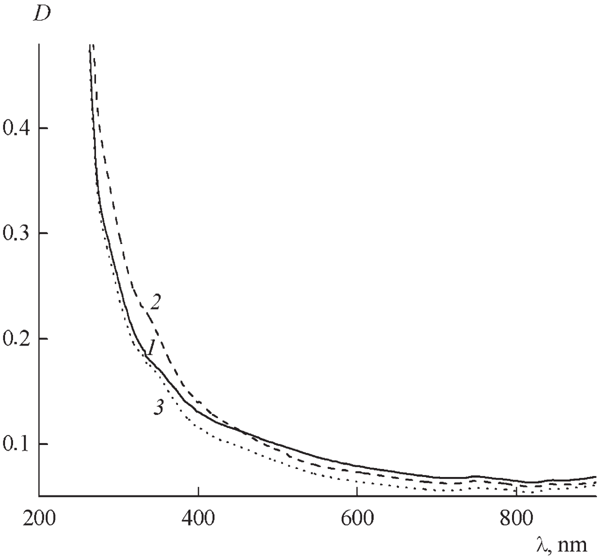

FIG. 9. UV spectra of the copolymer composite obtained at 1:1 (1), 1:2 (2) 2:1 (3) volume ratio of the aqueous B0 polymer solution and toluene solution of C_{60} isolated from water. The composite concentration was 10 mg per 1 ml of water. The thickness of the cell was 0.5 cm.

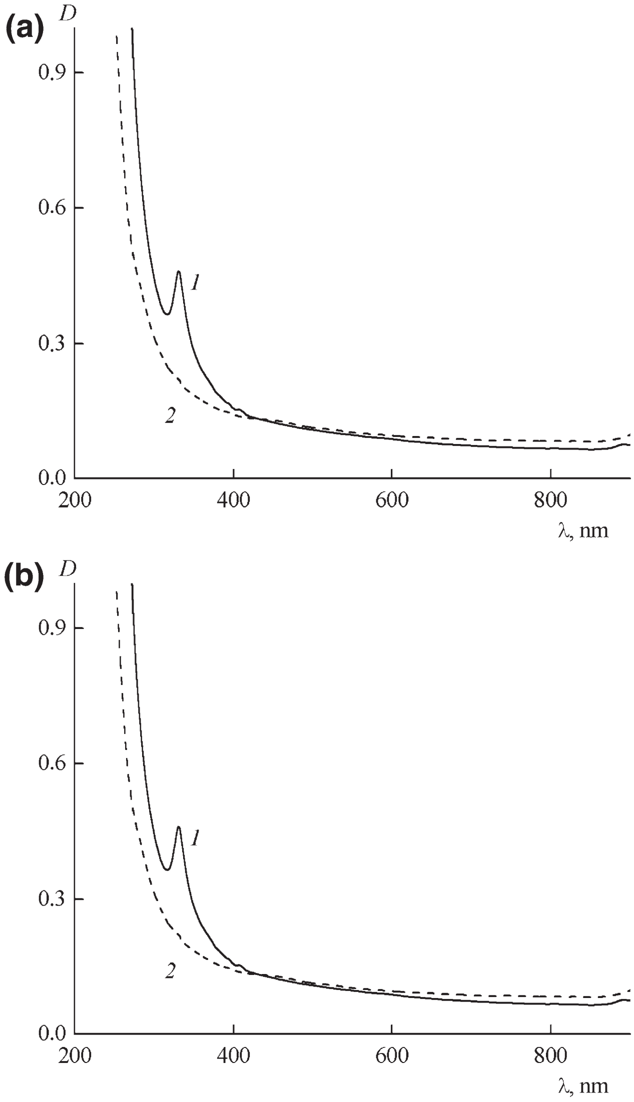

FIG. 10. (a) UV spectra of the polymer composite based on B5 (2:1) isolated from water in chloroform (1) and ethanol (2). (b) UV spectra of the copolymer composite based on B12 (1:1) isolated from water in chloroform (1), ethanol (2).

The L3-based composite (1:1) isolated from water can be dissolved easily in ethanol, water or chloroform. In all the case, their solutions were stable for several months: the C_{60} particles did not separate from solutions that indicate the formation of stable fullerene colloid in these solvents. Thus, isolated from water polymer composites based on L3, B0, B5 and B12 (co)polymers are soluble in water, ethanol and chloroform. The composites based on B0, B5 (1:1), and L3 (1:1) form stable colloidal solutions in water and ethanol.

CONCLUSIONS

It is shown that the copolymers of VP with DMTEG are suitable to encapsulate C_{60} from water-toluene mixtures of various compositions. In all experiments, the complex composition of amphiphilic copolymers was separated into two groups which are significantly different by solubility and compatibility with water and toluene. It is assumed that at mixing of colloidal aqueous solutions of (co)polymers and the fullerene solution in toluene two types of composites with different molecular structure of the polymer matrix, the fullerene content and particle size were produced. In a composite based on *N*-vinylpyrrolidone copolymer isolated from toluene the fullerene form larger particles, compare to that isolated from water. The stability of produced composites both in water and ethanol depends on the structure of the matrix and on the polymer:fullerene ratio. The polymer composites based on L3 polymer and B0, B5 copolymers primarily isolated from water are could be of considerable interest for biomedical applications. In this regard, the study on the structure and dynamics of copolymer$-C_{60}$ complex in water is an actual problem.

ACKNOWLEDGMENTS

The authors thank Prof. Atovmyan E.G. for helpful discussions.

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