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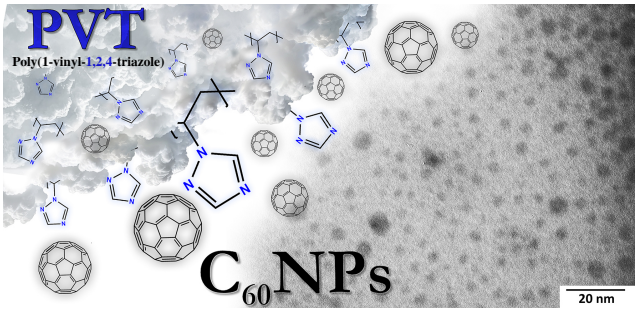
Aqueous dispersion of polymer-stabilized ultrasmall C_{60} fullerene nanoparticles

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An aqueous dispersion of C_{60} fullerene nanoparticles (up to 6 nm in size) has been obtained for the first time, with a C_{60} mass fraction of 4% relative to the hydrophilic poly(1-vinyl-1,2,4-triazole) added for the effective stabilization of the carbon nanoparticles. Nanoparticles of this size are formed as a result of donor–acceptor interactions between the triazole groups of the polymer and the C_{60} molecules, which act as cross-linking agents connecting the polymer chains. The ultrasmall size of the fullerene nanoparticles is crucial not only for biocompatibility but also for maintaining their photophysical properties in biological media.



Keywords: aqueous dispersion, ultrasmall nanoparticles, C_{60} fullerene, hydrophilic polymers, poly(1-vinyl-1,2,4-triazole), DLS, UV-VIS, TEM.

Fullerenes possess unique physical, chemical, electronic and optical properties and are in demand across various fields of science and technology.[1,2] This enables their use in addressing pressing challenges within high-tech sectors such as biomedicine, pharmaceuticals and cosmetology.[3,4] The most common and accessible fullerene is C_{60}, which exhibits promising antioxidant, photosensitizing and membranotropic properties.[5–9] However, the manifestation of its exceptional biological properties in aqueous solutions is complicated by aggregation and the formation of large C_{60} fullerene nanoparticles (C_{60}NPs), ranging from 350 to 500 nm in size, driven by the extremely high hydrophobicity of C_{60} molecules. Consequently, a key challenge in the application of fullerenes in medicinal chemistry is the development of stable water dispersions.

Covalent functionalization of C_{60} fullerene with hydrophilic moieties enhances its water solubility but leads to irreversible changes in properties critical for medical applications, including biocompatibility.[10] Modern supramolecular chemistry approaches enable the incorporation of C_{60} fullerene into various water-soluble compositions. Stable aqueous dispersions of C_{60} fullerene are prepared either by prolonged stirring in water or by solvent exchange (replacing an organic solvent with water) followed by ultrasonication. However, aqueous dispersions obtained *via* these methods exhibit the formation of large C_{60}NPs ranging from 50 to 500 nm in size; this indicates the occurrence of aggregation processes and results in low stability.[11–14]

Another, more promising approach involves the development of water-soluble systems based on C_{60} fullerene and hydrophilic polymers. This enables the production of aqueous C_{60} fullerene dispersions while preserving the properties that make it valuable for medical applications. For instance, incorporating C_{60} into hydrophilic polyvinylpyrrolidone yields the commercial product Radical Sponge®, which is used as a therapeutic agent to prevent aging and protect the skin from UV-induced damage. The size of C_{60}NPs in aqueous dispersions obtained in this manner is approximately 200 nm.[15,16]

Since the size and distribution pattern of C_{60}NPs, as well as the biological activity of their aqueous dispersions, depend significantly on the type of stabilizing polymer matrix, poly(1-vinyl-1,2,4-triazole) (PVT) was selected for the development of new aqueous C_{60} fullerene dispersions. PVT possesses valuable properties such as non-toxicity, hydrophilicity, biocompatibility, antimicrobial activity, sorption capacity, chemical and thermal stability, and film-forming ability.[17] It is important to note the high stabilizing capability of 1-vinyl-1,2,4-triazole-based polymers toward various metal nanoparticles, a property attributed to the formation of donor–acceptor complexes.[18,19] These properties make PVT a promising hydrophilic matrix for the effective stabilization of C_{60}NPs and the preparation of stable aqueous C_{60} fullerene dispersions.

This work demonstrates for the first time the possibility of obtaining an aqueous dispersion of C_{60} fullerene containing ultrasmall nanoparticles. A key feature of the selected system is the high stabilizing capacity of PVT. This enabled the preparation of an aqueous dispersion with a C_{60} fullerene content of up to 4 wt% relative to the polymer.

PVT–C_{60} dispersions were prepared by mixing solutions of C_{60} fullerene and PVT in *N*-methyl-2-pyrrolidone (NMP) under stirring,[20] followed by dialysis, and were characterized by dynamic light scattering (DLS), transmission electron microscopy (TEM), UV-visible spectroscopy (UV-VIS) and attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR).[†] Evaluation of the stability of the

[†] C_{60} fullerene with a purity of ~99.5% was obtained in-house at the A. E. Favorsky Irkutsk Institute of Chemistry. NMP, purified beforehand

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PVT–C_{60} dispersions in water showed no signs of sedimentation after three months of storage.

The hydrodynamic dimensions and optical properties of the aqueous PVT–C_{60} dispersion were determined using DLS and UV-VIS spectroscopy, respectively (Figure 1). Figure 1(*a*) shows that the resulting histograms exhibit a unimodal distribution. In the investigated aqueous PVT–C_{60} dispersion (0.1 mg ml^{-1}), the average hydrodynamic diameter is 40 nm, whereas the size of PVT macrocoils in the aqueous polymer solution is approximately 6 nm. The increase in the hydrodynamic dimensions of the dispersion particles compared to the pristine PVT indicates that the C_{60} fullerene acts as a cross-linking agent, connecting individual macrocoils and facilitating the formation of large PVT macromolecules.

In the UV-VIS spectra of the C_{60} solution in NMP [Figure 1(*b*)], intense absorption bands with maxima at 257 and 331 nm, characteristic of C_{60} fullerene, are observed. The C_{60} absorption band at 211 nm was not detected due to strong absorption by NMP at wavelengths below 260 nm. Absorption bands of C_{60} fullerene were also observed in the spectra of the PVT–C_{60} dispersion (at a concentration of 2.5 mg ml^{-1}), albeit with lower intensity, indicating the presence of C_{60} fullerene in the aqueous dispersion.

The size and distribution pattern of C_{60}NPs in the aqueous PVT–C_{60} dispersion were determined using TEM (Figure 2). Micrographs obtained at various magnifications clearly show electron-dense C_{60}NPs, predominantly spherical in shape and ultra-small in size (1 to 6 nm), uniformly distributed throughout the PVT polymer matrix. For comparison, an aqueous C_{60} dispersion prepared by dialyzing a C_{60} solution in NMP without stabilizing agents is characterized by a hydrodynamic particle size of 103 nm.[12] Thus, it can be concluded that the aqueous PVT–C_{60} dispersion is a colloidal system consisting of PVT macromolecular coils, within which ultrasmall carbon nanoparticles, acting as cross-linking agents, are uniformly distributed.

Aqueous dispersions of PVT and PVT–C_{60} were dried, lyophilized (60 °C, 0.05 mbar) and analyzed using ATR-FTIR spectroscopy to investigate the nature of the interaction between PVT and C_{60}NPs (Figure 3). A comparative analysis of the IR spectra of C_{60}, PVT and the lyophilized PVT–C_{60} nanocomposite revealed the following differences. The nanocomposite spectrum exhibits characteristic C_{60} bands at 526 and 1183 cm^{-1}

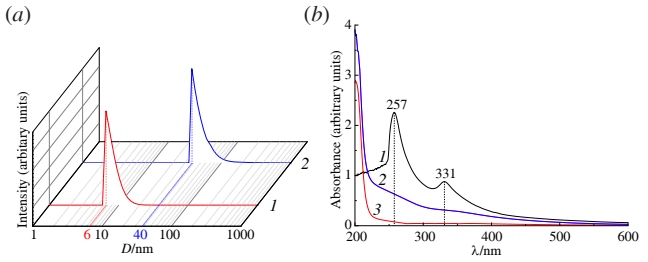


Figure 1 (*a*) Histograms of the hydrodynamic diameter distribution of scattering PVT particles in (*1*) water and (*2*) an aqueous PVT–C_{60} dispersion. (*b*) UV-VIS spectra of (*1*) C_{60} in NMP, (*2*) an aqueous PVT–C_{60} dispersion and (*3*) PVT in water.

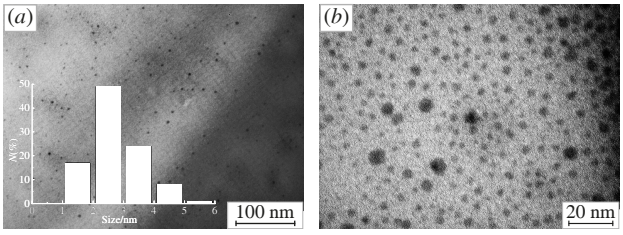


Figure 2 (*a*) TEM image with an overlaid histogram of the nanoparticle size distribution and (*b*) TEM image at higher magnification for an aqueous PVT–C_{60} dispersion.

(F_{1u} modes) that are absent in pure PVT. In the 520–530 cm^{-1} region, partial splitting of the C_{60} band is observed: instead of the single minimum characteristic of pure C_{60} (526 cm^{-1}), local minima at 526 and 529 cm^{-1} are detected in the composite, indicating a lifting of degeneracy due to reduced C_{60} symmetry upon interaction with PVT. Additionally, broadening of the C–N band in the 1432–1435 cm^{-1} region is observed, which may be attributed to partial overlap with the C_{60} band at 1428 cm^{-1}. These changes indicate an interaction between PVT and C_{60}. Given the presence of a lone electron pair on the pyridine-like nitrogen atom in the PVT heterocycle and the strong acceptor properties of C_{60}, the most likely mechanism is a donor–acceptor interaction involving possible partial charge transfer. Similar charge-transfer complex formation is observed in the interaction of C_{60} fullerene with polyvinylpyrrolidone.[21]

A comprehensive analysis of the results revealed that the hydrophilic PVT matrix possesses a high stabilizing capacity for C_{60}NPs. The uniform distribution of C_{60}NPs, with sizes up to 6 nm, within the PVT matrix prevented aggregation and preserved water solubility.

The results of this work demonstrate the first successful preparation of an aqueous dispersion of C_{60} fullerene stabilized by PVT in the form of ultrasmall nanoparticles. These findings contribute to a fundamental understanding of the formation processes of 'polymer–fullerene' hybrid systems by illustrating the influence of the stabilizer's nature on the size characteristics of the carbon nanoparticles. The combination of the polymer's biocompatibility and the functional properties of C_{60} fullerene in the synthesized PVT–C_{60} system offers significant potential for practical applications in theranostics, biosensor development and cosmetology, as well as in related fields of biomedicine and pharmacy.

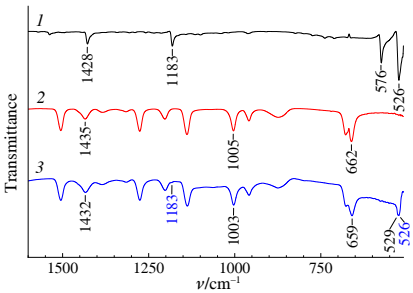


Figure 3 Comparison of ATR-FTIR spectra of (*1*) C_{60}, (*2*) PVT and (*3*) PVT–C_{60}.

by distillation and degassing, was used as the solvent. PVT with an average molecular weight of 98 kDa and a polydispersity index of 2.1 was synthesized in 78% yield *via* the radical polymerization of 1-vinyl-1,2,4-triazole, using azobisisobutyronitrile as the initiator. The molecular weight of PVT was determined using a Shimadzu LC-20 Prominence system equipped with a Shimadzu RID-20A refractive index detector and an Agilent PL1113-6500 column (PolyPore 7.5 × 300 mm).

In a dark glass vessel, a solution of C_{60} (0.01 g) in NMP (20 ml) was gradually mixed with a solution of PVT (0.25 g) in NMP (5 ml) under stirring.[20] Subsequently, to obtain an aqueous PVT–C_{60} dispersion, exhaustive dialysis against deionized water was performed for 48 h under stirring using a CelluSep H1 membrane with a 5 kDa pore size. Nitrogen content was determined by elemental analysis using a Flash EA 1112 Series instrument. Lyophilized samples (3–5 mg) of pure PVT and PVT–C_{60} were analyzed in triplicate. Since C_{60} contains no nitrogen, the mass fraction of C_{60} was calculated.

DLS analysis was performed using a ZetaPALS zeta-potential analyzer equipped with a BI-MAS module. UV spectroscopic analysis was carried out on a Shimadzu UV-2450 spectrophotometer. TEM images were obtained using a Titan Tecnai G2-20F S-TWIN FEI instrument. FTIR spectroscopic analysis was conducted on a Spectrum Two FTIR spectrometer using the ATR technique; the spectral resolution was 2 cm^{-1}.

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