

Research Article

Development and Characterization of Biocompatible Fullerene [C₆₀]/Amphiphilic Block Copolymer Nanocomposite

Alok Chaurasia,¹ Nanda Gopal Sahoo,² James T. McLeskey Jr.,³ and Xiao Hu¹

¹School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798

²Department of Chemistry, DSB Campus, Kumaun University, Nainital 263002, India

³Department of Physics, Randolph-Macon College, Ashland, VA 23005, USA

Correspondence should be addressed to Alok Chaurasia; ac_iitkgp@yahoo.com and Xiao Hu; axshu@ntu.edu.sg

Received 12 March 2015; Accepted 6 July 2015

Academic Editor: Pedro D. Vaz

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We report a supramolecular process for the synthesis of well-defined fullerene (C₆₀)/polymer colloid nanocomposites in an aqueous solution via complex formation. A biocompatible triblock poly(4-vinylpyridine)-*b*-polyethylene-*b*-poly(4-vinylpyridine), P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈, was synthesized by atom transfer radical polymerization. The block copolymer formed complexes with C₆₀ in toluene and resulted in fullerene assembly in cluster form. Nanocomposite dispersion in an aqueous solution could be obtained using an aged solution of the polymer/C₆₀/toluene solution by a solvent evaporation technique. The UV-Vis and FTIR spectroscopy confirmed the complex formation of fullerene with the polymer which plays a significant role in controlling the PDI and size of polymer/C₆₀ micelles in the toluene solution. The particle size and morphology of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ and P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ mixture were studied by dynamic light scattering (DLS) and transmission electron microscopy (TEM). In a cytotoxicity test, both pure polymer and the resulting polymer/C₆₀ composite in water showed more than 90% cell viability at 1 mg/mL concentration.

1. Introduction

The organization of fullerenes (C₆₀) and their derivatives into nanostructures within polymer systems has potential applications in solar cells and biomedicine [1–4]. For example, interesting results on polymer solar cells were reported using a blend of a fullerene derivative and a block copolymer poly(4-vinylpyridine) of poly(3-hexyl thiophene) (P3HT-*b*-P4VP) [5]. It was also found that a fullerene in an aqueous solution can generate a singlet oxygen under photoirradiation which has implications in the fields of biomedical and environmental science [4, 6]. One of the biologically most relevant features of C₆₀ is the ability to function as a “free radical sponge” and quench various free radicals more efficiently than conventional antioxidants [7]. Fullerenes also have widespread applications ranging from drug-delivery and tissue-scaffolding systems to consumer products [8], and they have been explored in the area of biological chemistry, for activities such as enzyme inhibition, antiviral activity, DNA cleavage, and photodynamic therapy [9].

However, many of C₆₀'s potential applications have been seriously hampered [10, 11] by its extremely low solubility in water. Derivatization of the fullerene molecule with various functional groups and other solubilization procedures using surfactants or long chain polymers [12, 13] through covalent interactions [14–17] may change the properties of C₆₀. It was reported that ¹O₂ quantum yield decreases with decreasing double bonds in the fullerene molecule due to the modification [18, 19]. Generally, introduction of any substituent into the fullerene core can diminish these properties [18–20]. A more effective and promising approach is to organize the fullerenes by specific noncovalent interactions with amphiphilic block copolymers through charge transfer complexation between fullerenes and block copolymers. Laiho and coworkers fabricated functionally unmodified C₆₀-containing nanostructures via a combination of PS-*b*-P4VP block copolymer self-assembly and charge-transfer complexation between fullerenes and P4VP segments in an organic solvent [21]. However, synthesis of water-soluble

adducts of this spherical carbon allotrope (potential biological applications) became a particularly challenging topic. Therefore, in order to enhance the processability and water solubility of the materials, self-assembly systems of pristine C_{60} with block copolymers have been explored. For example, water-soluble C_{60} /PS-*b*-PEO composites obtained through a tedious process exhibited multidistribution of particle sizes [22]. However, supramolecular aggregates with a more uniform size distribution could be obtained. This was done through the aggregation of C_{60} with PS-*b*-PDMAEMA in water using a dialysis process, where the fullerene preferably goes to PS region due to hydrophobic interaction [23]. However, in most cases, incorporation of fullerenes into water-soluble supramolecular structures using surfactants or other modifying agent results in the fullerene core being completely covered by the modifying agent. This reduces possibility of contact between water-soluble oxygen and fullerenes, thereby inhibiting some of the desired properties such as the ability to quench singlet oxygen (1O_2). Clearly, the preparation of well structure-defined aggregates from C_{60} with biocompatible polymers in an aqueous medium remains a challenge to overcome.

The present study focuses on the development of a simple method which will allow the assembly of fullerene with an amphiphilic block copolymer P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ in aqueous and organic media. The choice of the P4VP block is due to its more hydrophilic nature as compared to PS which will be more accessible to dissolved oxygen. The P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ amphiphilic block copolymer was synthesized using atom transfer radical polymerization [24, 25].

2. Materials and Methods

2.1. Chemicals and Materials. The hydroxy-end-capped PEO [degree of polymerization (DP): 105; PDI: 1.08] was purchased from Aldrich. 4-Vinylpyridine (VP) (99%) was purified by stirring over CaH_2 and distilled under vacuum. 2-Bromoisobutryl bromide, triethylamine, CuCl (99.99%), N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA 95%), and fullerene (99.5%) were purchased from Aldrich and used without further purification.

2.2. Charge Transfer Complex Formation. The triblock copolymer P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ was synthesized by using the ATRP method described elsewhere [26]. The polymer was dissolved in toluene (1 mg/mL) and kept stirring for 24 hrs. The fullerenes were separately dissolved in toluene with concentration of 1 mg/mL. The color of the solution was purple. The fullerene solution (1 mg/mL) was then added to polymer stock solution, keeping polymer and fullerene ratio of 95:5 (w/w). The initial color of solution was purple but with time it gradually turned into brown, indicates complex formation. The formation of the charge transfer complex as a function of time was monitored by UV-Vis spectrophotometry.

2.3. Preparation of Aqueous Colloidal Solution of Fullerene/Polymer Nanocomposite. The aqueous colloidal solution of

fullerene/polymer nanocomposite was obtained by pouring 10 mL of a two-month aged solution in toluene into 100 mL of water. The toluene was allowed to evaporate at 80°C for 6 hrs and the final volume of fullerene/polymer composite in aqueous solution was kept at 10 mL. No precipitation was observed.

2.4. In Vitro Cytotoxicity Test. An *in vitro* cytotoxicity test was performed to study the biocompatibility of the polymer, polymer/ C_{60} nanocomposite, in aqueous solution. For the cytotoxicity test, cell culture experiments were carried out using L929 mouse fibroblasts which were obtained from American Type Culture Collection (ATCC). Cells were grown in Dulbecco's modified Eagle's Medium (DMEM) supplemented with 10% heat inactivated Fetal Bovine Serum (FBS) (Lonza) and 1% Penicillin-Streptomycin-Glutamine (Antibiotic) (Gibco) maintained at 37°C in 5% CO₂ and 95% relative humidity. Cell cytotoxicity test was performed using the Promega CellTiter 96 AQueous One Solution Cell Proliferation Assay (MTS). This is a colorimetric method and the solution contains a tetrazolium compound [3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H tetrazolium] (MTS) and an electron coupling reagent (phenazine ethosulfate, PES). The compound is bio-reduced by living cells into a colored formazan product that is soluble in tissue culture medium. The quantity of formazan product is measured at 490 nm at which the intensity of absorbance is directly proportional to the number of living cells in culture [27–29]. Cells were seeded at a density of 2×10^4 cells/well in 96-well plates. After 24 hrs, culture medium was replaced by 200 μ L serial dilutions of the polymer solutions and the cells were incubated for 24 hrs. Polymer solutions were prepared in serum supplemented DMEM and sterilized by filtration (0.2 μ m). An MTS assay was done for four different concentrations, 0.1 mg/mL, 0.25 mg/mL, 0.5 mg/mL, and 1 mg/mL. At the end of incubation time period (24 hrs), polymer solutions were aspirated and replaced with 100 μ L fresh DMEM, to which 20 μ L CellTiter 96 AQueous One Solution was added. The cells were then incubated for 4 hrs at 37°C in 5% CO₂ incubator. Then the absorbance was measured at 490 nm in a microplate reader (TECAN, Tecan Group Ltd., Switzerland). The cell viability (%) related to control wells containing cell culture medium without polymer was calculated by $[A]_{\text{test}}/[A]_{\text{control}} \times 100$ equation. Each sample was done in triplicate.

2.5. Characterization. The Fourier Transform Infrared (FTIR) spectra were recorded on a Perkin Elmer system 2000. UV Spectrophotometer (UV2501PC, Pharmaspec, Shimadzu) was used to monitor the complex formation. Dynamic light scattering (DLS) [Nano Zetasize ZS90 (Malvern)] and transmission electron microscopy (TEM) (JEOL JEM-2010) were used to monitor the aggregation behavior.

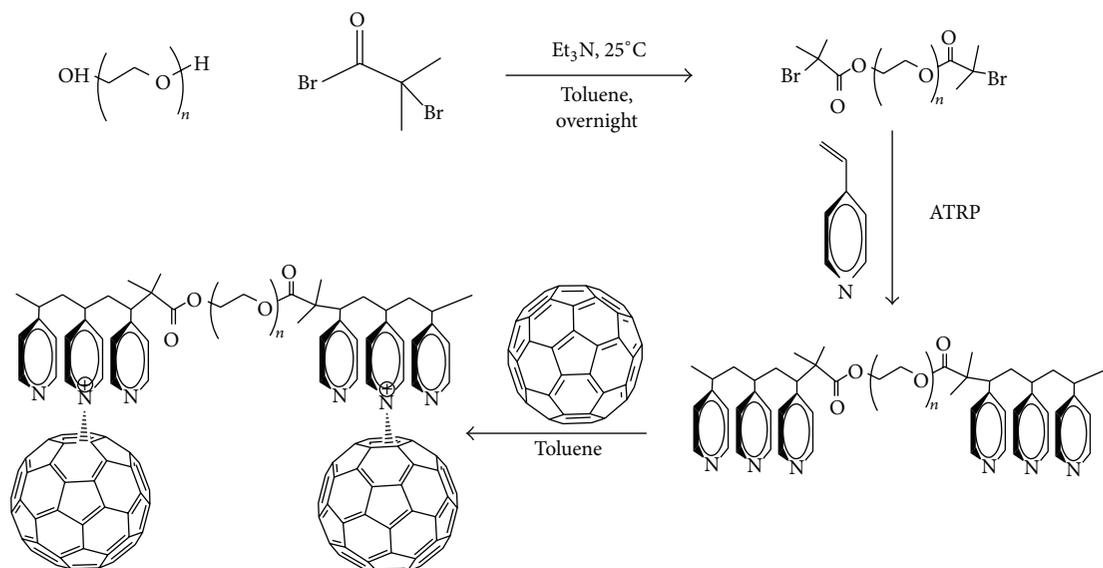


FIGURE 1: Scheme for synthesis of triblock copolymer and charge-transfer complex formation between P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ and C₆₀.

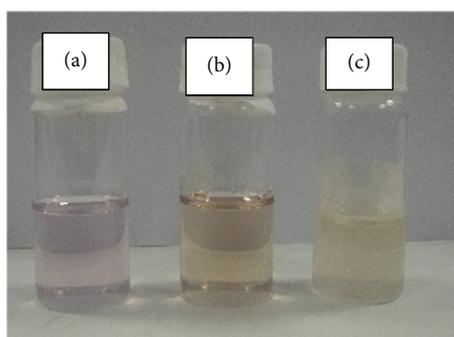


FIGURE 2: Colors of the solution for (a) freshly prepared P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ (95/5 w/w) in toluene, (b) two-month aged P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ (95/5 w/w), and (c) P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ (95/5 w/w) in water prepared from two-month aged solution by a solvent exchange process.

3. Results and Discussion

The block copolymer P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ was prepared via atom transfer radical polymerization (ATRP) and its complex with fullerene as outlined in Figure 1.

Fullerenes (C₆₀) dissolve readily in toluene, which leads to a purple color solution. A fullerene solution in toluene (1 mg/mL) was then added to polymer stock solution (1 mg/mL), keeping polymer fullerene ratio of 95 : 5 by weight. The initial color of solution was purple but with time it gradually turned into brown indicating complex formation as shown in Figure 2.

The color change with time was similar to that for the solution of C₆₀ in pyridine. This agrees with the formation of charge-transfer complexes between the electron-donating pyridine solvent and the electron-accepting fullerenes [30, 31]. The changes in the visible spectrum are shown in Figure 3. The solution shows a broad and weak absorption band ranging from 410 to 650 nm. The absorbance in the region

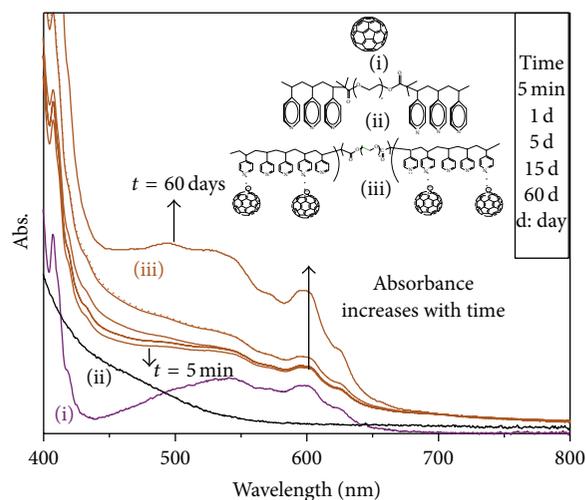


FIGURE 3: UV-Vis spectra of (i) C₆₀ in toluene, purple line, (ii) P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ in toluene, black line, and (iii) P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ (95/5 w/w) dissolved in toluene at different aging times (up to two months), brown line.

increases with aging. The spectral change (Figure 3(iii)) is attributed to the formation of charge transfer complex [30, 31].

In the solution of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ (95/5 w/w) the most characteristic absorption peak of fullerenes at ~332 nm was not observed. It is because, due to higher concentration of polymer/C₆₀ in solution, UV-Vis spectroscopy crosses the limit and was not able to pinpoint the most characteristic peak at ~332 nm. But the most characteristic peak at ~332 nm is clearly observed when the polymer/C₆₀ solution concentration was reduced by 50%, as it is shown in Figure 4.

FTIR spectroscopy provides further evidence for the complex formation. Upon aging of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ (95/5 w/w) in toluene, the pyridine peak at

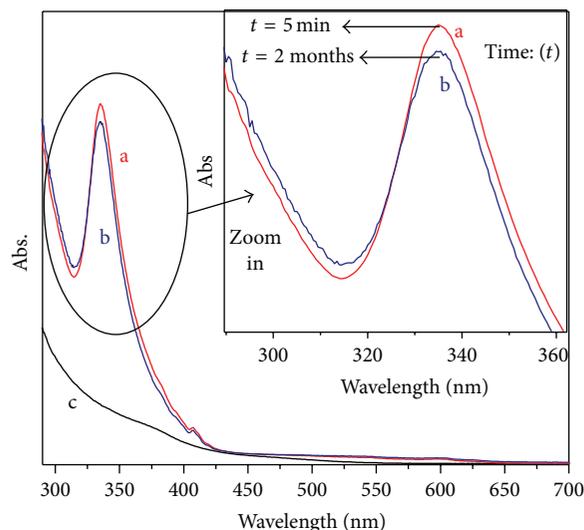


FIGURE 4: “a” line indicated UV-Vis spectrum of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ (95/5 w/w) dissolved in toluene (0.5 mg/mL) after 5 min aging; “b” line indicated UV-Vis spectrum of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ (95/5 w/w) dissolved in toluene (0.5 mg/mL) after 2-month aging; “c” line indicated UV-Vis spectrum of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ dissolved in toluene.

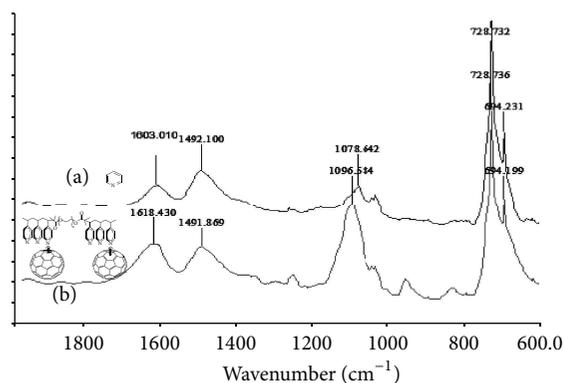


FIGURE 5: FT-IR spectra of (a) P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/toluene and (b) two-month aged solution of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ (95/5 w/w) in toluene.

1603 cm⁻¹ is slowly shifted to 1618 cm⁻¹ as shown in Figure 5. The shifting of the most characteristic peak due to interaction of the P4VP near 1600 cm⁻¹ for C=N stretching indicates that a slight electron transfer took place from the 4-vinylpyridine to C₆₀.

The UV-Vis spectrum of polymer/C₆₀ nanocomposite in an aqueous solution shows a broad peak from the fullerenes at about 340 nm. This peak clearly indicates the presence of fullerene in aqueous solution as shown in Figure 6.

The aggregation behavior of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ block copolymers was studied by dynamic light scattering using Zetasizer Nano ZS and ZS90 (Malvern). The apparent hydrodynamic radius (R_h) can be calculated using the Stokes-Einstein equation:

$$R_h = \frac{kT}{6\pi\eta D}, \quad (1)$$

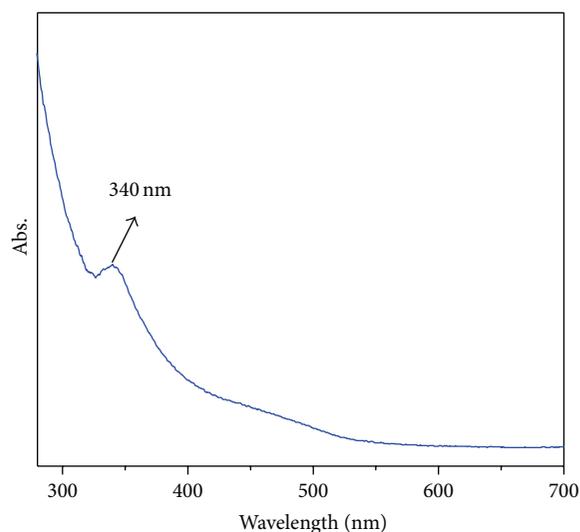


FIGURE 6: UV-Vis spectrum of polymer/C₆₀ nanocomposite in aqueous solution.

where k is the Boltzmann constant, T is the absolute temperature, η is the solvent viscosity, and D is the diffusion coefficient. The DLS was conducted at a scattering angle of 90°. The polymer in toluene solution (1 mg/mL) showed bimodal peaks with mean diameters of ~24.4 nm and ~199 nm, respectively, and the PDI was 0.534 (Figure 7(a)). The particle size ranges from 10 to 400 nm. However, in the presence of C₆₀ the polymer solution aggregates into one type of particle with mean diameter of 28.2 nm (Figure 7(b)) with PDI of 0.205. The particle size varies from 10 to 100 nm. The change in the aggregation behavior is clearly due to the C₆₀ complex formation.

TEM micrographs are shown in Figure 8. Figure 8(a) shows the micelle consisting of a compact P4VP core and

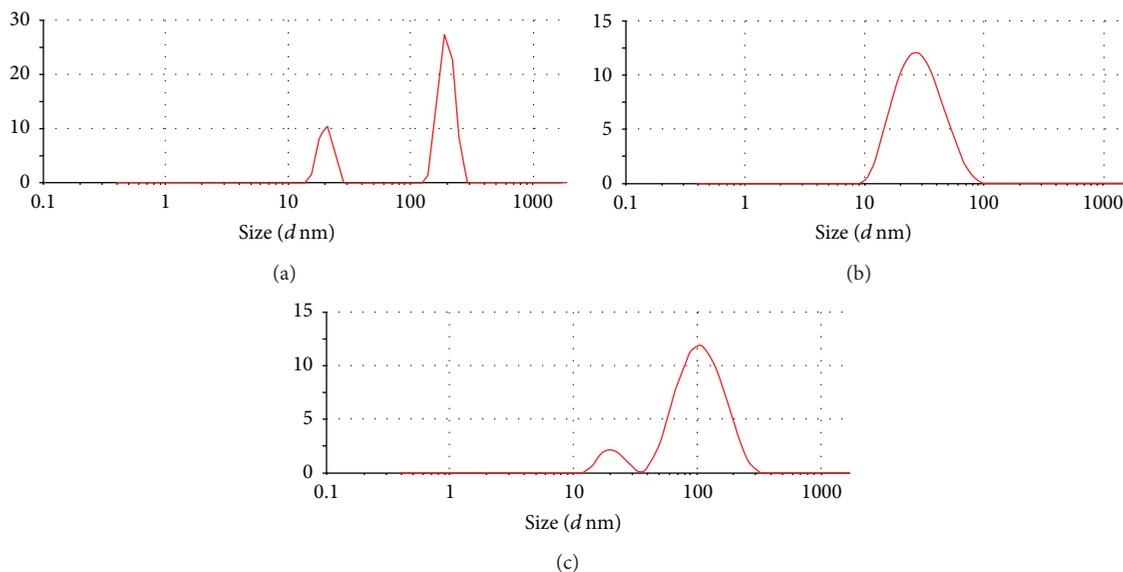


FIGURE 7: Dynamic light scattering of (a) $P4VP_8$ - b - PEO_{105} - b - $P4VP_8$ in toluene, (b) two-month aged $P4VP_8$ - b - PEO_{105} - b - $P4VP_8/C_{60}$ (95/5 w/w) in toluene, and (c) $P4VP_8$ - b - PEO_{105} - b - $P4VP_8/C_{60}$ nanocomposite in aqueous solution.

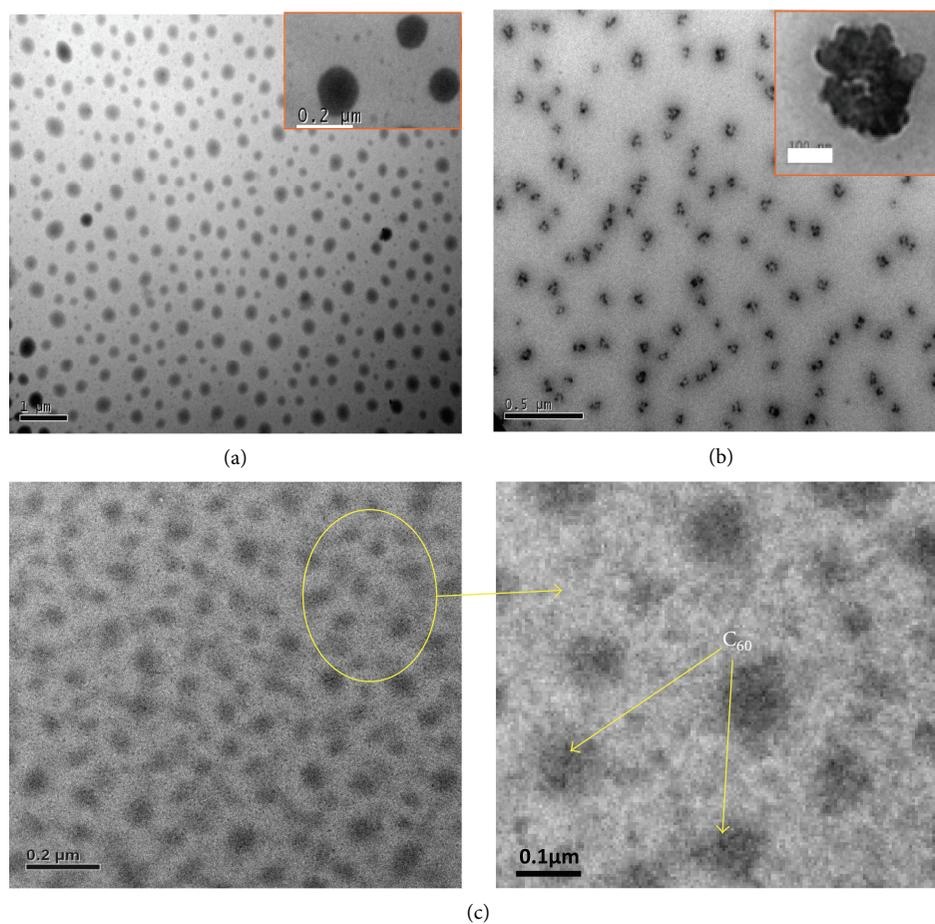


FIGURE 8: TEM images of (a) $P4VP_8$ - b - PEO_{105} - b - $P4VP_8$ in toluene with iodine stain, (b) aged $P4VP_8$ - b - PEO_{105} - b - $P4VP_8/C_{60}$ (95/5 w/w) in toluene solution (scale bar: 500 nm) without iodine staining, (c) fullerene cluster from aqueous solution (200 nm), and zoom in form of "c" where fullerene clusters are visible (100 nm), images were taken without iodine staining.

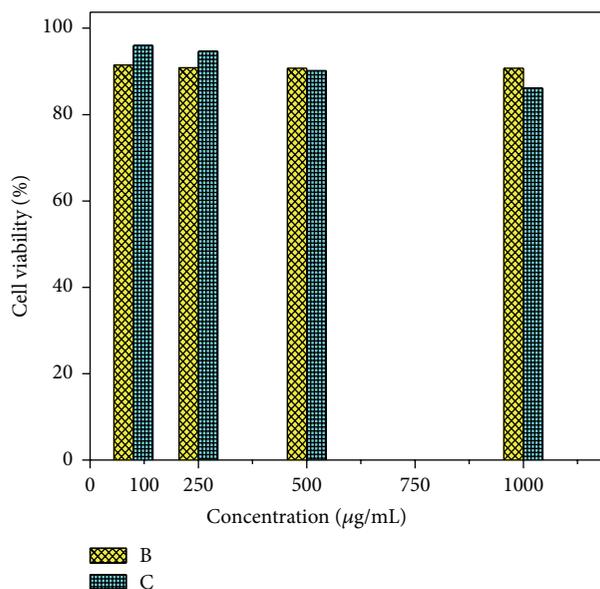


FIGURE 9: *In vitro* cytotoxicity studies of (B) polymer in water and (C) polymer/ C_{60} nanocomposite in water.

PEO chains as the corona. These samples were stained with iodine. On the other hand, the polymer/fullerene composites in toluene and water are shown in Figures 8(b) and 8(c), respectively, without iodine staining. The lack of iodine staining was to avoid confusion between P4VP and fullerene which shows up clearly in the fullerene aggregates. The particle size from TEM studies is in good agreement with the light scattering data for the P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ polymer and C_{60} complexes.

From the TEM, it was determined that the C_{60} clusters were aggregated with a size of ~30 nm. In light scattering studies (Figure 7(c)), the polymer/ C_{60} nanocomposite micelle in aqueous solution shows the bimodal distribution with mean diameters of ~30 nm and ~110 nm. This agrees reasonably well with the TEM images. The TEM images confirm the formation of fullerene clusters in both processes. The results confirm that the micelle in solution consists of P4VP in the core and PEO in the corona. The fullerenes are located in the core of the polymer aggregates. A plausible mechanism of the micelle formation of P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ and P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/ C_{60} (95/5 w/w) is shown in Scheme 1.

To evaluate the possibility of using the pure polymer and the polymer/ C_{60} nanocomposite in aqueous solution for bioapplications, *in vitro* cytotoxicity studies were performed by MTS assay. This is a colorimetric test, based on the selective ability of viable cells to reduce the tetrazolium component of MTS into purple colored formazan crystals. MTS assay was done for four different concentrations, namely, 0.1 mg/mL, 0.25 mg/mL, 0.5 mg/mL, and 1 mg/mL. The results (Figure 9) show that there is no significant cytotoxicity of the four different concentrations of the pure polymer and the polymer/ C_{60} nanocomposite. It was found that more than 90% of the cells are viable in all the different concentrations for both cases.

4. Conclusions

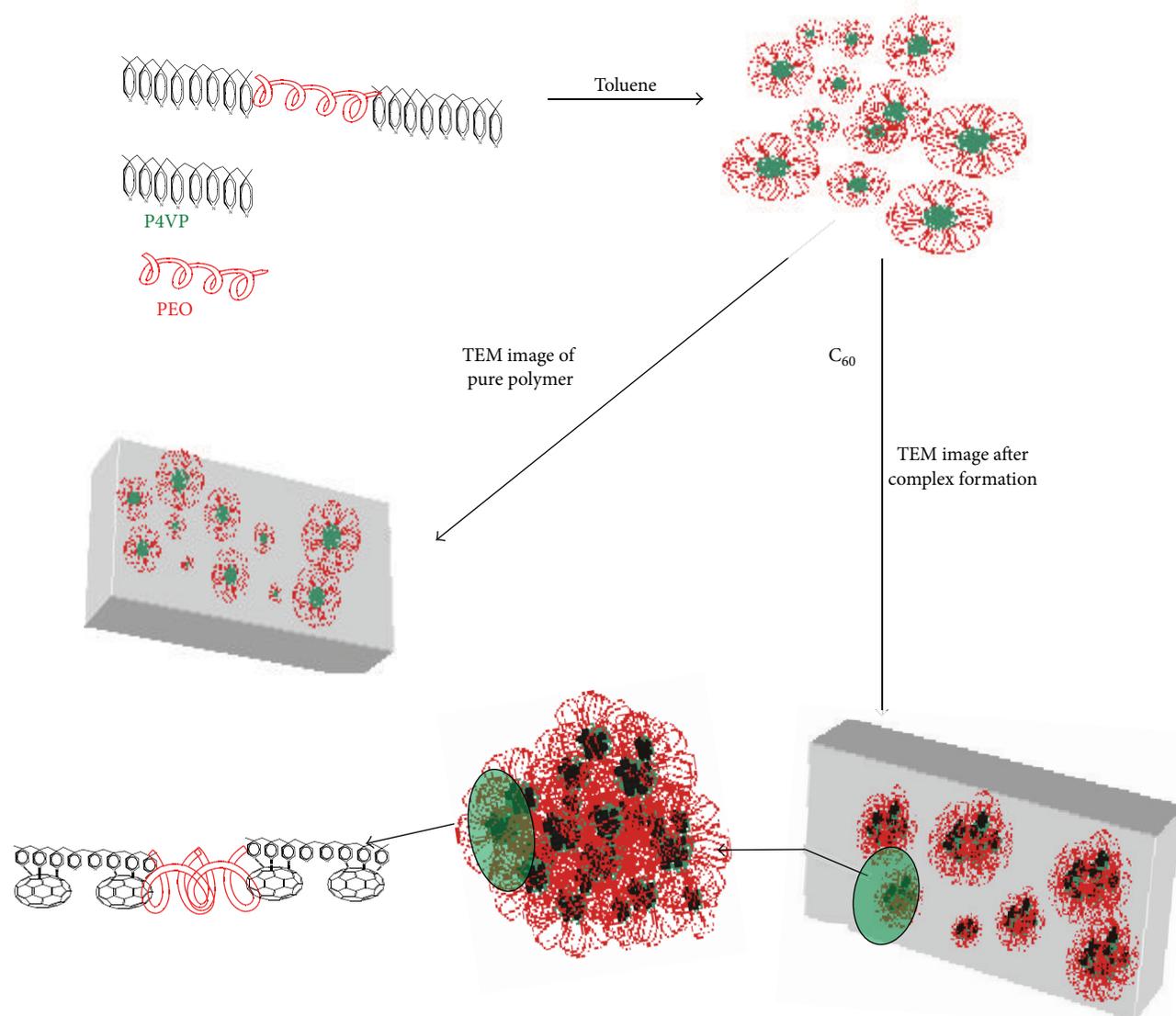
This study shows that P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/ C_{60} systems can lead to the formation of self-assembled structures. The C_{60} complexation process has significant effect on the aggregation behaviour. Upon aging of the solution, a charge transfer complex between vinylpyridine unit and C_{60} was formed, which leads to the formation of self-assembled fullerene clusters. These results were supported by UV-Vis, TEM, and DLS studies. The formation of biocompatible P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/ C_{60} nanocomposites in water may have potential application in biomedicine, cosmetic (as singlet oxygen generator) or other useful applications. In summary, organic-soluble and water-soluble, structurally well-defined C_{60} /polymer nanocomposites were achieved through the self-assembly of pristine C_{60} with polymer. Though the rate of complex formation presented in this study was found to be slow, the work has opened the door and enlightened how noncovalent interaction can be used to obtain water-soluble, biocompatible, polymer-fullerene nanoparticles.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors acknowledge funding from National Research Foundation of Singapore under a competitive research program (NRF-G-CRP-2007-01). One of the authors (Alok Chaurasia) would like thank Nanyang Technological University for a graduate scholarship.



SCHEME 1: Plausible mechanism of the micelle formation in P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈ and P4VP₈-*b*-PEO₁₀₅-*b*-P4VP₈/C₆₀ (95/5 w/w).

References

- [1] L.-M. Chen, Z. Hong, G. Li, and Y. Yang, "Recent progress in polymer solar cells: manipulation of polymer: fullerene morphology and the formation of efficient inverted polymer solar cells," *Advanced Materials*, vol. 21, no. 14-15, pp. 1434–1449, 2009.
- [2] R. Po, M. Maggini, and N. Camaioni, "Polymer solar cells: recent approaches and achievements," *The Journal of Physical Chemistry C*, vol. 114, no. 2, pp. 695–706, 2010.
- [3] N. S. Sariciftci, D. Braun, C. Zhang et al., "Semiconducting polymer-buckminsterfullerene heterojunctions: diodes, photodiodes, and photovoltaic cells," *Applied Physics Letters*, vol. 62, no. 6, pp. 585–587, 1993.
- [4] M. Orfanopoulos and S. Kambourakis, "Chemical evidence of singlet oxygen production from C₆₀ and C₇₀ in aqueous and other polar media," *Tetrahedron Letters*, vol. 36, no. 3, pp. 435–438, 1995.
- [5] N. Sary, F. Richard, C. Brochon et al., "A new supramolecular route for using rod-coil block copolymers in photovoltaic applications," *Advanced Materials*, vol. 22, no. 6, pp. 763–768, 2010.
- [6] J. L. Anderson, Y.-Z. An, Y. Rubin, and C. S. Foote, "Photo-physical characterization and singlet oxygen yield of a dihydrofullerene," *Journal of the American Chemical Society*, vol. 116, no. 21, pp. 9763–9764, 1994.
- [7] P. J. Krusic, E. Wasserman, P. N. Keizer, J. R. Morton, and K. F. Preston, "Radical reactions of C₆₀," *Science*, vol. 254, no. 5035, pp. 1183–1185, 1991.
- [8] Z. Markovic and V. Trajkovic, "Biomedical potential of the reactive oxygen species generation and quenching by fullerenes (C₆₀)," *Biomaterials*, vol. 29, no. 26, pp. 3561–3573, 2008.

- [9] A. S. Boutorine, H. Tokuyama, M. Takasugi, H. Isobe, E. Nakamura, and C. Hélène, "Fullerene-oligonucleotide conjugates: photoinduced sequence-specific DNA cleavage," *Angewandte Chemie*, vol. 33, no. 23-24, pp. 2462–2465, 1995.
- [10] C. C. Zhu, Y. Xu, Y. Q. Liu, and D. B. Zhu, "Preparation and characterization of novel amphiphilic C₆₀ derivatives," *Journal of Organic Chemistry*, vol. 62, no. 7, pp. 1996–2000, 1997.
- [11] P. Ravi, S. Dai, K. M. Hong, K. C. Tam, and L. H. Gan, "Self-assembly of C₆₀ containing poly(methyl methacrylate) in ethyl acetate/decalin mixtures solvent," *Polymer*, vol. 46, no. 13, pp. 4714–4721, 2005.
- [12] W. T. Ford, T. Nishioka, S. C. McCleskey, T. H. Mourey, and P. Kahol, "Structure and radical mechanism of formation of copolymers of C₆₀ with styrene and with methyl methacrylate," *Macromolecules*, vol. 33, no. 7, pp. 2413–2423, 2000.
- [13] S. Mehrotra, A. Nigam, and R. Malhotra, "Effect of [60]fullerene on the radical polymerization of alkenes," *Chemical Communications*, no. 5, pp. 463–464, 1997.
- [14] H. Yu, L. H. Gan, X. Hu, S. S. Venkatraman, K. C. Tam, and Y. Y. Gan, "A novel amphiphilic double-[60]fullerene-capped triblock copolymer," *Macromolecules*, vol. 38, no. 23, pp. 9889–9893, 2005.
- [15] J.-F. Nierengarten, M. Gutiérrez-Nava, S. Zhang et al., "Fullerene-containing macromolecules for materials science applications," *Carbon*, vol. 42, no. 5-6, pp. 1077–1083, 2004.
- [16] Z. T. Ball, K. Sivula, and J. M. J. Fréchet, "Well-defined fullerene-containing homopolymers and diblock copolymers with high fullerene content and their use for solution-phase and bulk organization," *Macromolecules*, vol. 39, no. 1, pp. 70–72, 2006.
- [17] K. Sivula, Z. T. Ball, N. Watanabe, and J. M. J. Fréchet, "Amphiphilic diblock copolymer compatibilizers and their effect on the morphology and performance of polythiophene: fullerene solar cells," *Advanced Materials*, vol. 18, no. 2, pp. 206–210, 2006.
- [18] T. Hamano, K. Okuda, T. Mashino et al., "Singlet oxygen production from fullerene derivatives: effect of sequential functionalization of the fullerene core," *Chemical Communications*, no. 1, pp. 21–22, 1997.
- [19] D. M. Guldi and K.-D. Asmus, "Photophysical properties of mono- and multiply-functionalized fullerene derivatives," *Journal of Physical Chemistry A*, vol. 101, no. 8, pp. 1472–1481, 1997.
- [20] F. Prat, R. Stackow, R. Bernstein, W. Qian, Y. Rubin, and C. S. Foote, "Triplet-state properties and singlet oxygen generation in a homologous series of functionalized fullerene derivatives," *The Journal of Physical Chemistry A*, vol. 103, no. 36, pp. 7230–7235, 1999.
- [21] A. Laiho, R. H. A. Ras, S. Valkama, J. Ruokolainen, R. Österbacka, and O. Ikkala, "Control of self-assembly by charge-transfer complexation between C₆₀ fullerene and electron donating units of block copolymers," *Macromolecules*, vol. 39, no. 22, pp. 7648–7653, 2006.
- [22] X. L. Chen and S. A. Jenekhe, "Solubilization and encapsulation of fullerenes by amphiphilic block copolymers," *Langmuir*, vol. 15, no. 23, pp. 8007–8017, 1999.
- [23] X.-S. Wang, T. Metanawin, X.-Y. Zheng, P.-Y. Wang, M. Ali, and D. Vernon, "Structure-defined C₆₀ polymer colloids supramolecular nanocomposites in water," *Langmuir*, vol. 24, no. 17, pp. 9230–9232, 2008.
- [24] S. N. Sidorov, L. M. Bronstein, Y. A. Kabachii et al., "Influence of metalation on the morphologies of poly(ethylene oxide)-block-poly(4-vinylpyridine) block copolymer micelles," *Langmuir*, vol. 20, no. 9, pp. 3543–3550, 2004.
- [25] H. Yu, L. H. Gan, X. Hu, and Y. Y. Gan, "A pH-sensitive double [60]fullerene-end-capped polymers via ATRP: synthesis and aggregation behavior," *Polymer*, vol. 48, no. 8, pp. 2312–2321, 2007.
- [26] C. Alok, L. H. Gan, and X. Hu, "Dramatic solvent effect on interaction kinetics and self-organization of phenyl-C₆₁ butyric acid methyl ester in a triblock copolymer," *Macromolecular Chemistry and Physics*, vol. 212, no. 8, pp. 813–820, 2011.
- [27] T. M. Buttke, J. A. McCubrey, and T. C. Owen, "Use of an aqueous soluble tetrazolium/formazan assay to measure viability and proliferation of lymphokine-dependent cell lines," *Journal of Immunological Methods*, vol. 157, no. 1-2, pp. 233–240, 1993.
- [28] T. Mosmann, "Rapid colorimetric assay for cellular growth and survival: application to proliferation and cytotoxicity assays," *Journal of Immunological Methods*, vol. 65, no. 1-2, pp. 55–63, 1983.
- [29] G. Malich, B. Markovic, and C. Winder, "The sensitivity and specificity of the MTS tetrazolium assay for detecting the in vitro cytotoxicity of 20 chemicals using human cell lines," *Toxicology*, vol. 124, no. 3, pp. 179–192, 1997.
- [30] S. Bhattacharya, S. K. Nayak, S. Chattopadhyay, M. Banerjee, and A. K. Mukherjee, "Study of molecular complex formation between [60]fullerene and two series of donors by the NMR method," *The Journal of Physical Chemistry A*, vol. 105, no. 43, pp. 9865–9868, 2001.
- [31] S. Bhattacharya, S. K. Nayak, S. K. Chattopadhyay, M. Banerjee, and A. K. Mukherjee, "Absorption spectroscopic study of EDA complexes of [70] fullerene with a series of methyl benzenes," *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy*, vol. 57, no. 2, pp. 309–313, 2001.



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