

Double Stimuli-Responsive Copolymer Stabilizers for Multiwalled Carbon Nanotubes

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S Supporting Information

ABSTRACT: A unique copolymer stabilizer is presented that can be used to stabilize multiwalled carbon nanotubes in aqueous solution to form “smart” dispersions. They showed double stimuli-responsive behavior (in dependence of temperature and ionic strength) and allowed for accurate control of the transition (exfoliated → agglomerated) temperature of nanotubes over a wide temperature range. In spite of its effective dispersion strength, the copolymer was easily synthesized in one step via free radical copolymerization of *N*-isopropylacrylamide and 1-ethyl-3-vinylimidazolium bromide.



Carbon nanotubes (CNTs) show unusual electrical, mechanical, optical, thermal, and chemical properties. Since their discovery in 1991, they have drawn widespread attention and interest in the field of nanoscience and nanotechnology.¹ Their application spectrum is very broad, including nanoelectronics,² drug delivery,³ composite devices of different types,⁴ optical sensors,⁵ and many more. When CNTs are produced or processed, they agglomerate readily into bundles because of hydrophobic interactions, representing a severe obstacle in realizing full application potential, because agglomeration forfeits some inherent properties and reduces heavily the interfacial interaction. A solution to this problem is to disperse CNTs homogeneously using a stabilizer and deagglomeration agent. This process can be divided into two steps, that is, exfoliation of CNT bundles into individual tubes and keeping them separated in a solvent phase.

Two state-of-the-art modification techniques are known, namely, the “covalent” and the “physical” approaches. The former is based on surface modifications typically involving the covalent attachment of a molecule to the CNT surface to solubilize them in a given solvent.^{6,7} Conversely this may undesirably disrupt the extended π -networks on the CNT, diminishing both the mechanical and electronic performance. The latter, the physical method, relies on mixing of CNTs with a strongly interacting but excessively applied stabilizer,^{8–10} but is often advantageous as it preserves the original physical properties of CNTs. In such a method, organic molecules or polymers are thus far the most popular candidates. For instance, pyrene-based surfactants, DNAs, and others have been widely applied.^{11–17}

Stimuli-responsive polymers are sensitive to variations in their external environments, and adopt their conformation accordingly. In nature this phenomenon helps biological systems regulate mass transport, convert signals, and so on.^{18–20} Such polymers are playing an increasingly important role in a diverse range of research areas, including drug delivery, diagnostics, (bio)sensing, separation, and “smart” coatings. Although rarely reported, stimuli-responsive polymers have been exploited to disperse CNTs in solution. It gives rise to

“smart” CNT dispersions that could respond to environmental perturbation. For example, a common pH responsive polymer, poly(acrylic acid), was used to control the exfoliation and bundling of SWNTs in aqueous solution via the changes in conformation and degree of ionization introduced by pH.^{21,22} Copolymers of poly(*N*-cyclopropylacrylamide) or poly(*N*-isopropylacrylamide) (PNIPAM) with a small fraction of pyrene side groups could generate stable aqueous dispersions of SWCNTs that were sensitive to temperature.^{23,24} In another example, photo- and thermal-responsive polymers composed of alternating units of azobenzene and phenylene or vinylene units were used as dispersants for SWNTs, however, in nonaqueous media.²⁵

In this contribution a novel type of temperature and ionic strength responsive MWCNT dispersion in aqueous media is reported, employing a unique copolymer stabilizer prepared via free radical polymerization of NIPAM and an ionic liquid monomer, 1-ethyl-3-vinylimidazolium bromide (EVImBr, content: 2.2–12.8 mol %). These two monomers were selected as PNIPAM is a well-known thermosensitive polymer with a low critical solution temperature (LCST) of 32 °C, close to human body temperature, while PEVImBr is a poly(ionic liquid) that can disperse CNTs by strong polarization interactions and responds to ionic strength in solution.^{26–29} As discussed, these factors can be synergistically combined in the copolymer poly(NIPAM-*co*-EVImBr), generating an even more efficient stabilizing system for MWCNTs, producing double stimuli-responsive dispersions. In turn, CNT dispersions can then be precipitated in a wide range of specific, predetermined temperatures.

In this work, dispersing MWCNTs was accomplished by sonicating MWCNTs and copolymers in aqueous media at room temperature. A homogeneous, dark dispersion developed and was stable for months without precipitation. Transmission

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electron microscopy (TEM) and cryogenic TEM (Cryo-TEM) characterization of the aqueous dispersion of MWCNTs was conducted to illustrate the close-to-perfect state of dispersion (Figure 1A,B). Large-sized agglomerates of MWCNTs are

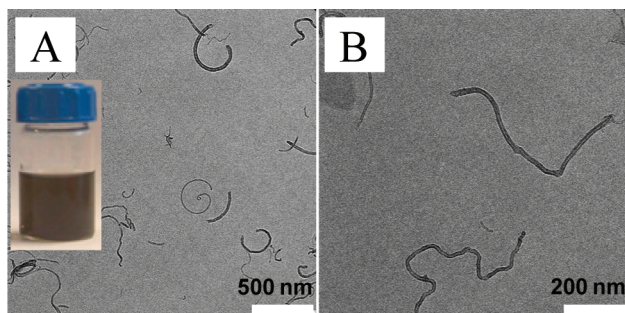
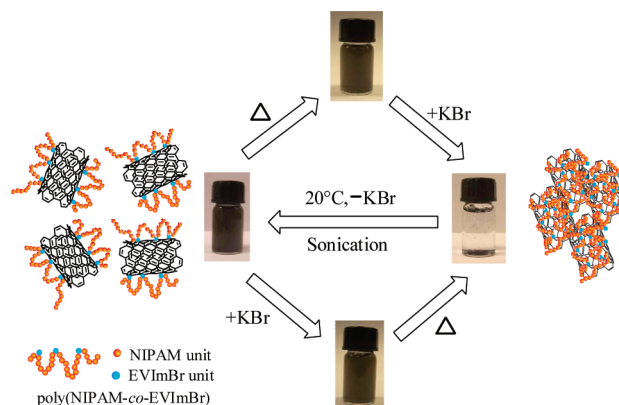


Figure 1. Representative TEM images of dispersed MWCNTs (0.02 wt %) in aqueous solution using poly(NIPAM-*co*-EVI_mBr) (0.4 wt %; EVI_mBr content ~7.6 mol %) as stabilizer. Inset (A) is a photograph of the formed stable dispersion of MWCNTs, taken 24 h after sonication treatment.

essentially absent, presenting well disentangled dispersions, independent of length and diameter. Furthermore, Cryo-TEM measurements demonstrate that in a real solution state the MWCNTs are indeed well-dispersed, even at a high local concentration (Figure S8 in the SI). Thus, the presence of the copolymer stabilizer facilitated deagglomeration of the hydrophobic MWCNTs via sonication and the formation of a homogeneous aqueous dispersion. The solubilizing effect is believed to stem from the PEVI_mBr fraction in the copolymer chain. It has been widely reported that imidazolium-containing molecules and polymers are effective dispersants for CNTs.^{30–35} On the contrary, there is only a modest or insufficient interaction between MWCNTs and PNIPAM. This can be supported by a control experiment in which the same procedure was performed to MWCNTs, except PNIPAM homopolymer was used instead of the copolymer. Precipitation was found shortly after the sonication and completed within 24 h (Figure S9 in the SI).

Besides acting as stabilizer, poly(NIPAM-*co*-EVI_mBr) is in fact a double stimuli-responsive polymer due to the sensitivity of PNIPAM against temperature and that of PEVI_mBr against ionic strength. As MWCNTs are solubilized in aqueous media solely by this copolymer, their dispersions inherit such responsiveness. Scheme 1 shows the photographs and structural model of the aqueous MWCNT dispersion in different environments. At room temperature, the PEVI_mBr units are preferentially attached to the MWCNT surface, and the PNIPAM linkers stretch into the solution to stabilize MWCNTs. Through heating to 60 °C or adding excessive KBr salt, the dispersion remains stable. That is, collapse of either PNIPAM at elevated temperature or PEVI_mBr at high salt concentration resulted in colloidal stability, reflective of two understandable scenarios. If PNIPAM collapses, the PEVI_mBr fraction still holds MWCNTs in solution via charge stabilization, while slating out the PEVI_mBr fraction still leaves the steric stabilization. Only the combination of heating and salt leads to complete destabilization of MWCNTs. The precipitated MWCNTs can be redispersed at 20 °C via the assistance of sonication, provided that the salt supernatant is removed. Thus, nanotubes suspended in a copolymer solution can be switched between an exfoliated and a bundled state

Scheme 1. Schematic Illustration of Temperature and Ionic Strength Responsive MWCNT Dispersion by Using a Copolymer Stabilizer



when the temperature and salt effects are applied together; referred to here as the “double key system”.

A deeper insight of the intrinsic responsiveness presented by the MWCNT dispersion was obtained via investigating the solution behavior of the copolymer stabilizer alone through temperature-dependent UV/vis turbidity measurements at different salt concentrations (Figure 2). A turbidity curve of

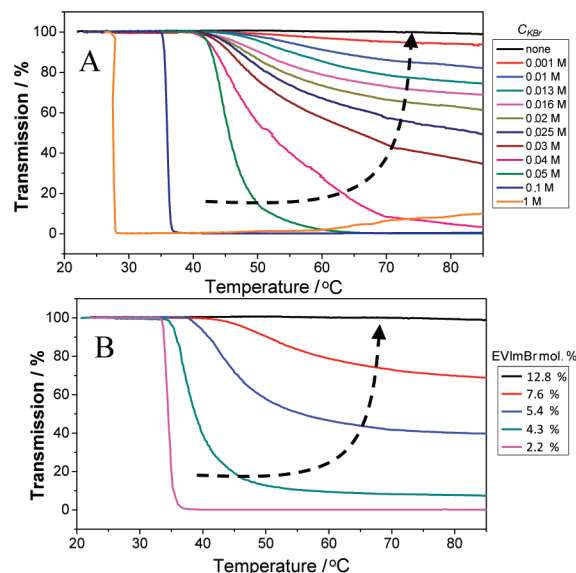


Figure 2. Turbidity curves (transmission vs temperature) of aqueous solutions (10 g/L) of poly(NIPAM-*co*-EVI_mBr) with 7.6 mol % of EVI_mBr and different concentrations of KBr (A), and with different EVI_mBr monomer unit content and a constant concentration of KBr ($C_{\text{KBr}} = 0.015\text{ M}$; B).

the copolymer solution at diverse KBr concentrations from 0 to 1 M was recorded (Figure 2A). Without added salt ($C_{\text{KBr}} \sim 0$), the copolymer solution remains wholly transparent even at 90 °C. The PNIPAM chains become hydrophobic above the LCST and are, therefore, adequately solubilized by the charged PEVI_mBr component. In the presence of KBr, a cloud point (here defined as 80% of the transmission) appears and gradually shifts to lower temperatures. At a sufficiently high concentration ($C_{\text{KBr}} \sim 0.04\text{ M}$), the copolymer starts to precipitate out above 70 °C, that is, macroscopic phase separation takes place. Upon a further increase in salt

concentration from 0.1 and 1.0 M, there is a distinct transition at a low temperature of 25–40 °C. This salt effect is due to the low solubility of the PEVImBr fraction at high KBr concentrations according to ordinary solubility product rules.^{26,36} Apart from ionic strength, the chemical composition in the copolymer also plays an important role in determining its temperature-dependent solution behavior. Figure 2B shows the turbidity curve of the copolymer with various EVImBr content at a constant salt concentration, $C_{\text{KBr}} \sim 0.015$ M. The copolymer with 12.8 mol % of EVImBr remains stable, and the turbidity is almost constant in the whole temperature range. Along a decreasing EVImBr content gradient, a transition step appears and becomes more pronounced. It is worth mentioning that at the lowest PEVImBr content (2.2 mol %), the copolymer shows a transition step at 35 °C, very close to that of pure PNIPAM, but can still efficiently stabilize MWCNTs, as shown later. Indeed, by variation of salt concentration and chemical composition the transition temperature of the copolymer in solution can be easily controlled.

The intrinsic solution behavior of the copolymer stabilizer governs that of the MWCNTs in dispersion. This provides a unique chance to manipulate the MWCNTs from a well-exfoliated to aggregated state over a wider temperature range (Figure S10 in SI). The freedom in both the temperature and ionic strength domains to tune the dispersion state of CNTs provides a strong mechanism means to design task-specific CNT dispersions. Figure 3 presents an example to prepare

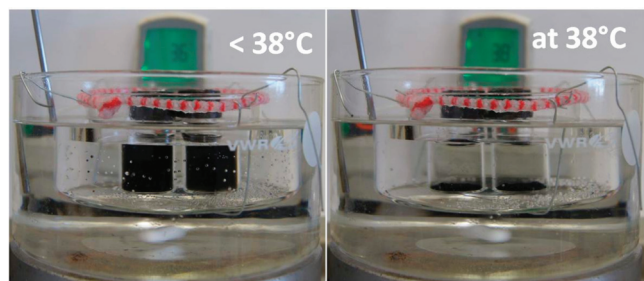


Figure 3. Destabilization of MWCNTs in aqueous solution at a specific temperature. Left: samples at a temperature lower than 38 °C; right samples at 38 °C. In each photograph, in the left vial, the copolymer stabilizer contained 7.6 mol % of EVImBr, $C_{\text{KBr}} \sim 0.1$ M; in the right one, it contained 2.2 mol % of EVImBr, $C_{\text{KBr}} \sim 0.013$ M.

MWCNT dispersions that precipitate at a specific temperature. The left vial is an aqueous dispersion of MWCNTs stabilized at $C_{\text{KBr}} \sim 0.1$ M by a copolymer with 7.6 mol % of EVImBr; the right one at $C_{\text{KBr}} \sim 0.013$ M with 2.2 mol % of EVImBr. In spite of the different compositions of copolymer stabilizers, the MWCNT dispersions show an identical transition temperature at 38 °C. What matters here are the different salt concentrations in these two vials. They were carefully chosen to independently shift the transition temperatures of MWCNTs, which differentiate from each other at the same KBr concentration (as shown in Figure 2B) to exactly the same temperature. Described more elegantly, this precipitation event is designable.

In conclusion, a new, simple-to-make polymer stabilizer that enables the generation of “smart” waterborne dispersions of carbon nanotubes that respond to both temperature and ionic strength in solution was presented. Our experiments clearly illustrate the benefit of using such a copolymer as a multifunctional stabilizer; one can tune the aqueous stability

of CNTs over a wide temperature range and control destabilization precisely at a desired temperature. Equally significant, this approach can be expanded to other aromatic carbon nanostructures, like fullerenes and graphenes, as the intrinsic polarizable cation– π interaction holds true for all carbon nanostructures.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and some characterization are presented. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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