Self-Assembly of Pluronic Block Copolymers in Aqueous Dispersions of Single-Wall Carbon Nanotubes as Observed by Spin Probe EPR

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The self-assembly of Pluronic block copolymers in dispersions of single-wall carbon nanotubes (SWNT) was investigated by spin probe electron paramagnetic resonance (EPR) spectroscopy. Nitroxide spin labeled block copolymers derived from Pluronic L62 and P123 were introduced in minute amounts into the dispersions. X-band EPR spectra of the SWNT dispersions and of native polymer solutions were measured as a function of temperature. All spectra, below and above the critical micelle temperature (CMT), were characteristic of the fast limit motional regime. The temperature dependence of the ^{14}N isotropic hyperfine coupling, a_{iso}, and the rotational correlation time, τ_c, were determined. It was observed that, below the CMT, EPR does not distinguish between chains adsorbed on SWNT and free chains. Above CMT, substantial differences were observed: in the native solution, the Pluronics spin labels experience only one environment, S_m, assigned to spin labels in the corona of the Pluronic micelle, whereas in the SWNT dispersions, in addition to S_m, a second population of nonaggregated, individual chains, S_i, is observed. The relative amounts of S_m and S_i were found to depend on the relative concentrations of the Pluronic and SWNT. Furthermore, the aggregates formed in the SWNT dispersions do not show the typical increase in chain-end mobility as a function of temperature, observed in the post-CMT regime of the native Pluronic solutions. This suggests a larger dynamical coupling among aggregated chains in the presence of the SWNT as compared to the native micelles. The overall findings are consistent with the formation of a new type of aggregates, composed of a SWNT-polymer hybrid.

Introduction

Self-assembly (SA) of polymers and nanostructures is of much interest as it may serve as a leading pathway for preparation of new types of structural functional materials.[1,2] Driven by the interplay between different intermolecular forces, SA is dominated by interactions with typical energies of the order of the thermal energy. Thus, the process is reversible and sensitive to the presence of additives.[3,4] Nanostructures constitute a class of additives that combine molecules and colloidal lengthscales. It is expected that they would affect the phase behavior, dynamics, and mechanisms of self-association in the combined polymer–nanostructures–solvent systems. Detailed characterization of those systems, from the molecular to the macroscopic level, is an important prerequisite for utilization of SA, yet it provides a difficult challenge for both experiment and theory.

In this study, we focus on SA of amphiphilic block copolymers poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), $PEO_nPPO_mPEO_n$ (Poloxamers (ICI) or Pluronics (BASF)). Pluronics block copolymers are known to self-assemble in water into micelles consisting of a hydrophobic core of PPO and a corona of the solvated PEO.[4] It is accepted that the driving force

for micellization in aqueous solutions is entropic.[4,5] Micellization of Pluronics is initiated (at a fixed temperature) by increasing the concentration to above a critical concentration, CMC, or by increasing the temperature (at a given concentration) to above a critical temperature, CMT.[4,6] Here we investigate the molecular details of copolymers SA from aqueous solutions in the presence of single-wall carbon nanotubes (SWNT) by spin probe electron paramagnetic resonance (EPR) spectroscopy. SWNT are cylindrical structures with a typical diameter of 0.8–2 nm and length of up to millimeters, resulting in a large aspect ratio (>1000) and a relatively large surface area.[7] Furthermore, they are hydrophobic and are characterized by a large and nonisotropic polarizability.[7] While in previous studies we characterized the effect of Pluronic block copolymers on the solution behavior of SWNT,[8–10] here we focus on the effect of SWNT on the process of Pluronics SA and the formation of aggregates, as observed via spin probe EPR. The EPR studies were complemented by information obtained via differential scanning calorimetry (DSC).[11]

Spin probe EPR is a well-established technique; nitroxide spin labels are routinely used in systems where no paramagnetic center is present. The EPR spectrum of the spin label provides

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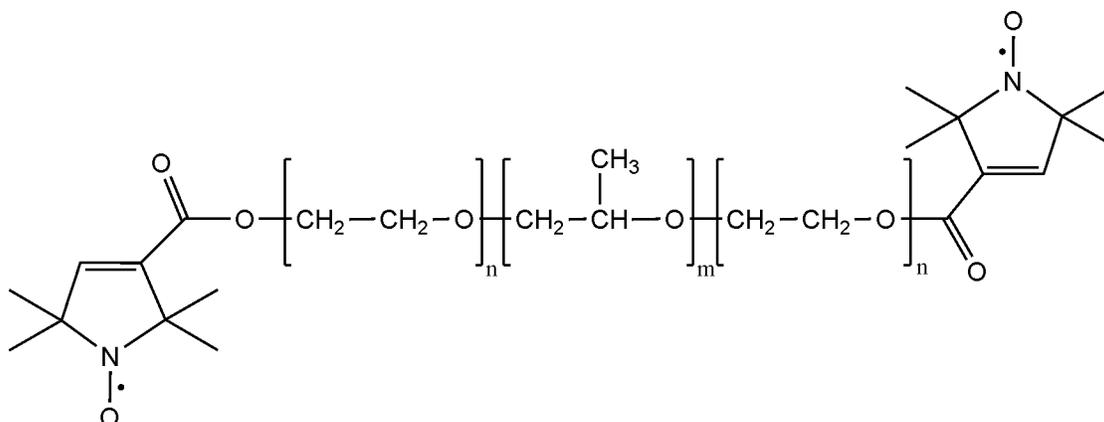
(1) Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418–2421.

(2) Boncheva, M.; Whitesides, G. M. *MRS Bull.* **2005**, *30*, 736–742.

(3) Steinbeck, C. A.; Hedin, N.; Chemelka, B. F. *Langmuir* **2004**, *20*, 10399–10412 and references therein.

(4) *Amphiphilic Block copolymers Self-assembly and Applications*; Alexandridis, P., Lindman, B., Eds.; Elsevier: Amsterdam, 2000.

(5) Maibaum, L.; Dinner, A. R.; Chandler, D. *J. Phys. Chem. B* **2004**, *108*, 6778–6781.

(6) Wanka, G.; Hoffman, H.; Ulbricht, W. *Macromolecules* **1994**, *27*, 4145–4159.

(7) Dresselhaus, M. S.; Dresselhaus, G.; Avouris, Ph. *Carbon nanotubes: synthesis, structure, properties, and applications;* Springer-Verlag: Berlin, 2001; Vol. 80.

(8) Shvartzman-Cohen, R.; Nativ-Roth, E.; Baskaran, E.; Levi-Kalisman, Y.; Szleifer, I.; Yerushalmi-Rozen, R. *J. Am. Chem. Soc.* **2004**, *126*, 14850–14857.

(9) Shvartzman-Cohen, R.; Levi-Kalisman, Y.; Nativ-Roth, E.; Yerushalmi-Rozen, R. *Langmuir* **2004**, *20*, 6085–6088.

(10) Nativ-Roth, E.; Shvartzman-Cohen, R.; Bounioux, C.; Florent, M.; Zhang, D.; Szleifer, I.; Yerushalmi-Rozen, R. *Macromolecules* **2007**, *40*, 3676–3685.

(11) Shvartzman-Cohen, R.; Florent, M.; Goldfarb, D.; Szleifer, I.; Yerushalmi-Rozen, R. *Langmuir*, in press.

Scheme 1

information on its motional characteristics in terms of rotational correlation times, its anisotropy, and its order parameter, which reflect the properties of its environment.[12] Moreover, the polarity of a spin label's microenvironment can be probed by the isotropic ^{14}N hyperfine coupling, a_{iso}, which decreases when the polarity of the environment decreases[12] and therefore can be used to detect processes such a micellization.[13,14] As micellization of Pluronics is associated with a change in polarity and mobility, a careful choice of spin probes can provide a reliable indication on different stages of the process.[16,17,18]

As was demonstrated before, nitroxide spin probe that are covalently attached to the terminal hydroxyl of each PEO chain (see Scheme 1) exhibit an EPR spectrum that is sensitive to the motion of the PEO tails.[16,17,18]

By labeling Pluronic block copolymers of different PEO–PPO ratio, it is possible to target the spin label to different regions in the forming micelles (or aggregates) and obtain comprehensive information on the aggregation process and the nature of the formed aggregates.[16,17]

In this study, we investigated SA and aggregation in SWNT dispersions, as a function of temperature, of two Pluronic block copolymers, P123 ($m = 70, n = 20$) and F127 ($m = 70, n = 106$) that differ in the length of the PEO block. As was shown before,[8–10] the dispersions are formed by physical adsorption of Pluronic chains to the nanotubes, via the PPO moiety, in the single-chain (below CMT) regime. Here, we focus on the onset of SA, induced by increasing the temperature, and follow via spin probe EPR the transition to the micellar regime. The usage of two probes that differ in the length of the PEO and PPO blocks allows us to map different regimes of the forming aggregates.

Our findings suggest that in the presence of dispersed SWNT, SA and aggregation occur on the nanotubes and result in the formation of a polymer–SWNT hybrid structures.

Experimental

Materials. *Polymers.* Two different water soluble Pluronic triblock copolymers were received as a gift from BASF AG Germany and used as received (Table 1).

(12) Schneider, D. J.; Freed, J. H. In *Spin labeling: theory and applications*; Berliner, L. J., Reuben, J., Eds.; Biologiclal Magnetic Resonance; Plenum: New York, 1989; vol. 8, Chapter 1.

(13) Morisett, J. D. *Spin labeling: theory and applications*; Academic Press: New York, 1976; Chapter 8.

(14) Caldararu, H. *Spectrochim Acta, Part A* **1998**, *54*, 2309–2336.

(15) Caragheorgheopol, A.; Caldararu, H. *Electron Paramagnetic Resonance*; The Royal Society of Chemistry: Cambridge, UK, 2000: Vol. 17, p. 205.

(16) Caragheorgheopol, A.; Caldararu, H.; Dragutan, I.; Joela, H.; Brown, W. *Langmuir* **1997**, *13*, 6912–6921.

(17) Ruthstein, S.; Frydman, V.; Kababya, S.; Landau, M.; Goldfarb, D. *J. Phys. Chem. B*, **2003**, *107*, 1739–1748.

(18) Ruthstein, S.; Frydman, V.; Goldfarb, D. *J. Phys. Chem. B* **2004**, *108*, 9016–9022.

Table 1. Composition of PEO–PPO–PEO Copolymers

polymer	M_w	no. of EO units (n)	no. of PO units (m)	PEO (wt %)	product no.
P123	5750	20	70	30	587 440
F127	12 600	106	70	70	583 106

Raw SWNT synthesized by arc discharge were purchased from Carbolex Inc., U.S.A. (SWNT (AP) http://carbolex.com) and used as received. According to the specifications by the manufacturer, the as-prepared AP grade consists of 50–70 vol % SWNT, graphite, cobalt, and nickel (ca. 20 nm in diameter).

The spin labeled Pluronics used were L62-NO and P123-NO, and they were synthesized as described in the literature.[16]

Sample Preparation. Aqueous solutions of the block copolymers were prepared by dissolving a block copolymer in water at room temperature (22–24 °C) to form solutions of 1 wt %. The solutions were mixed for about 2–3 days using a magnetic stirrer. An appropriate volume of a 5–10 mM stock solution of the spin probe in ethanol was added to a vial, and then the solvent was evaporated, leaving solid spin probe in the vial. Then, an appropriate volume of the 1 wt % Pluronic solution was added to this vial and the sample was left under stirring overnight to ensure that the spin probe has dissolved. Liquid dispersions of SWNT were prepared by sonicating 1 wt % of the raw material at very mild conditions (50 W, 43 kHz) for 30–40 min in the 1 wt % polymeric solution with the spin probe. The dispersions were centrifuged (at 4500 rpm for 30 min) and the supernatant was decanted from above the precipitate. As was shown before,[8] the dispersion process is selective toward SWNT, and the precipitate mainly contains colloidal moieties. Yet, we estimate that some of the SWNT would precipitate. Therefore, the actual weight percent of the dispersed SWNT is lower than the initial concentration (1 wt %), designated throughout the text. Because a reliable and established method that would provide the actual concentration of
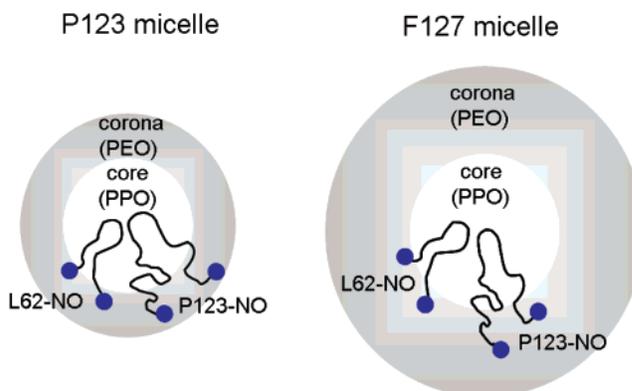

Figure 1. A schematic representation of the location of the spin labels of L62-NO and P123-NO in micelles of P123 and F127.

Table 2. The a_{iso} and τ_c Values of L62-NO and P123-NO in Solutions of 1 wt % P123 and 1 wt % F127 below (285 K) and above CMT (345 K)

		a_{iso} (mT) 285 K	τ_c ($\times 10^{-10}$s) 285 K	a_{iso} (mT) 345 K	τ_c ($\times 10^{-10}$s) 345 K
L62-NO	1 wt % P123	1.591 ± 5E-3	1.38 ± 0.02	1.478 ± 5E-3	2.3 ± 0.02
	1 wt % F127	1.594 ± 5E-3	1.37 ± 0.02	1.502 ± 5E-3	2.46 ± 0.02
P123-NO	1 wt % P123	1.599 ± 5E-3	1.28 ± 0.02	1.501 ± 5E-3	3.27 ± 0.02
	1 wt % F127	1.598 ± 5E-3	1.25 ± 0.02	1.519 ± 5E-3	1.99 ± 0.02

dispersed carbon nanotubes in dispersions of either ionic surfactants or polymeric solutions is still unavailable (see Supporting Information in ref 10), we have focused on relative concentrations that can be controlled. In order to control the relative concentration of SWNT and polymers, we adopted the following procedure: stock dispersions of SWNT in a given polymer were prepared. When required, solutions of lower relative SWNT concentration were obtained by diluting the stock dispersion with 1 wt % polymeric solution with spin probe. Dispersions of higher relative polymer concentration were prepared by dissolving in the existing dispersion additional polymer, up to the desired concentration. This allowed us to study the effect of the Pluronic/SWNT ratio independently on the actual concentration of dispersed SWNT.

Techniques and methods. *Spin Probe EPR.* EPR spectra were recorded using X-band Bruker Elexsys 500 spectrometer with a modulation amplitude of 0.3G. The samples were introduced in two quartz capillaries (0.80 i.d. × 1.0 o.d.) wrapped with Teflon tape and the temperature was controlled using the spectrometer temperature controller. For temperatures lower than room temperature, the sample was cooled by N_2 gas passed through an acetone/dry ice bath. The actual temperature was precalibrated by a thermocouple located at the center of the cavity. Spectra were recorded while increasing and decreasing the temperature, with equilibration periods of 30 min between each step. Comparison of the heating and cooling sequences showed that the measurements are reversible and do not exhibit hysteresis.

The measured EPR spectra were all in the fast limit region. When only one species was present in solution, the correlation time, τ_c (in sec), was derived from the relative intensities and width of the EPR lines according to the relation[19]

$$\tau_c = (6.51 \times 10^{-10})\Delta H(0)\{[h(0)/h(-1)]^{1/2} + [h(0)/h(1)]^{1/2} - 2\} \quad (1)$$

where $\Delta H(0)$ is the peak-to-peak line width (in Gauss) of the central line ($M_I = 0$) of the nitroxide spectrum and $h(-1)$, $h(0)$ and $h(1)$ are the peak-to-peak heights of the $M_I = -1, 0$, and $+1$ lines, respectively. When two species were present, the spectra were simulated using Easyspin,[20] and τ_c and a_{iso} were derived from least-square fitting of the spectra.

Results

Dispersions of individual SWNT were prepared following the previously published procedure[8-10] (see also Supporting Information). EPR measurements of Pluronic native solutions and of SWNT dispersions containing two spin probes were carried out as a function of temperature. The two spin probes used in this study are based on L62 ($m = 30$, $n = 5$), referred to as L62-NO, and P123 ($m = 70$, $n = 20$), referred to as P123-NO (see Scheme 1). Thermal measurements of solutions and dispersions containing spin labeled Pluronic have shown that the presence of the labels does not perturb the system (see Supporting Information).

As the two spin probes differ in the length of the PEO and PPO blocks, the nitroxide label resides at a different location within a micelle of a given Pluronic. In Figure 1, we present a schematic showing the location of the two spin probes, as has

been inferred from the a_{iso} value and ^{2}H modulation depth in three-pulse electron-spin echo envelope modulation (ESEEM) traces in micellar solutions of P123 in D_2O.[17,18] Lower a_{iso} value, lower ^{2}H modulation depth, and higher τ_c value for L62-NO as compared to P123-NO indicate that in the micelles of P123 the nitroxide group of L62-NO is close to the core−corona interface while that of P123-NO is closer to the corona−water interface (Figure 1).[17,18] In F127 micelles, which have a longer PEO block, both probes experience a somewhat more polar environment. Table 2 lists the a_{iso} and τ_c values of the two spin probes in the various solutions at 285 K, below the CMT, and 345 K, above the CMT.

In Figure 2a, we present the temperature dependence of the EPR spectra of L62-NO in aqueous solutions of 1 wt % P123. The spectra below the CMT represent a single species in the fast motion regime, referred to as S_i. Micellization is clearly identified between 297 and 312 K by a reduction in a_{iso} and an increase in line width. During the transition, two species are observed, one assigned to spin probes in the micelles, S_m, and the other is assigned to individual chains in solution, S_i. The temperature dependence of a_{iso} and τ_c, derived using eq 1 is shown in Figure 3 a,b; both experience a significant change at the CMT. The a_{iso} values of S_m decrease as the temperature above the CMT increases, indicating a reduction in the hydrophilic character of the PEO chains, as expected.[21]

The temperature dependence of the EPR spectra of L62-NO in SWNT dispersed in 1 wt % P123 is shown in Figure 2b. The main difference between the SWNT dispersion and the native solution is that while in the latter one species is observed below and above the CMT two environments are detected above CMT
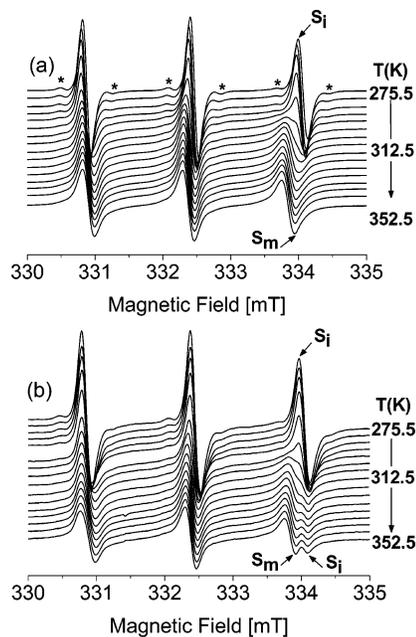

Figure 2. Temperature dependence of the EPR spectra of L62-NO in 1 wt % P123: (a) the native solution; (b) a dispersion of 1 wt % SWNT. Features corresponding to S_i (single chains) and S_m (micellized chains) are indicated. The signals marked with ∗ are due to ^{13}C hyperfine splittings. Spectra were recorded every 5 K.

(19) Stone, T. J.; Buckman, T.; Nordio, P. L.; McConnell, H. M. *Proc. Natl. Acad. Sci. U.S.A.* **1965**, *54*, 1010−1017.
(20) Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 42−55.
(21) Alexandridis, P.; Athanassiou, V.; Hatton, T. A. *Langmuir* **1995**, *11*, 2442−2450.
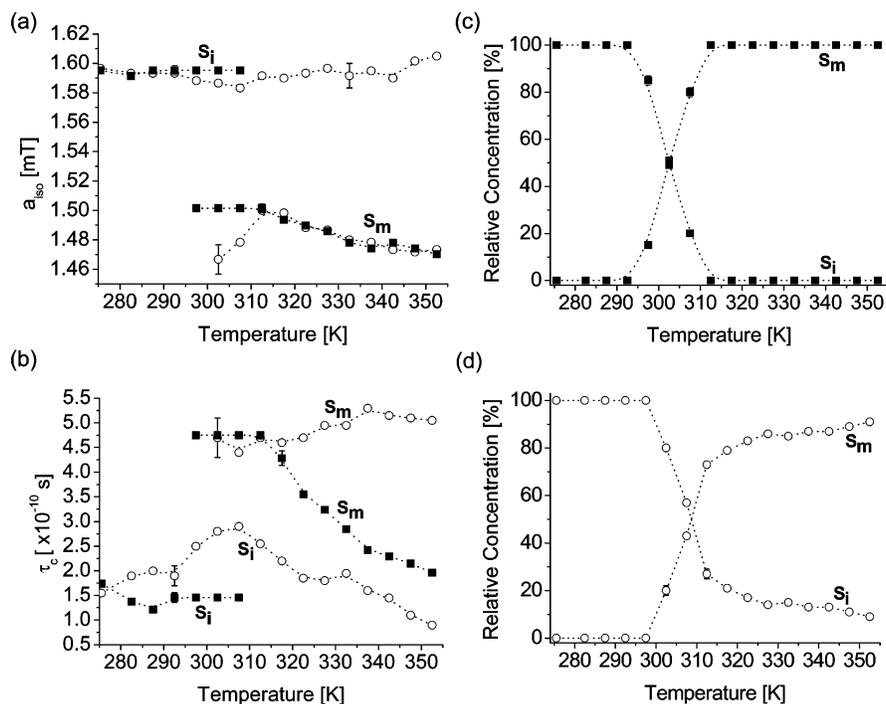
Figure 3. Temperature dependence of (a) a_{iso} and (b) τ_c of L62-NO in 1 wt % P123 solutions: (■) no SWNT; (○) dispersions of 1 wt % SWNT. The relative amounts of S_i and S_m as a function of temperature for (c) the native solution and (d) the SWNT dispersion. A typical error bar is presented.

in the SWNT dispersion (Figure 3c,d). One is characteristic of a spin probe within micelles similar to the one observed in the native solution, S_m, while the other is characterized by values of the parameters that are typical of individual chains in solution below CMT, S_i. The fact that the two signals are well resolved at all temperatures tested above the CMT indicates that there is no exchange between the polymer chains in the micelles and in the solution within the EPR time scale ($<10^{-6}$ sec).

The a_{iso} and τ_c values of the two species and their relative amount were determined from simulations (Figure 4), and their temperature dependence is depicted in Figure 3. These results show that SA of Pluronic chains also takes place in the SWNT dispersion. Furthermore, the majority of the L62-NO probes ($\sim$80%) are located within the formed aggregates, whereas a minor amount ($\sim$20%) is attributed to individual nonaggregated chains. An interesting observations is that τ_c of S_m at the posttransition regime is practically temperature independent, showing a qualitatively different behavior from that observed in the native solutions, where τ_c decreases as the temperature is raised. Also the τ_c of S_i is somewhat higher for the dispersions. The latter observation indicates that the interaction of the micelles with the SWNT dominates over the temperature effect. Unlike τ_c, the behavior of a_{iso} was similar in the native solutions and the SWNT dispersions, indicating that in the region of the spin label the water content of the aggregates formed in the presence of SWNT is similar to that of the native micelles.

To obtain further information regarding the partitioning of L62-NO between the two environments, we explored how their relative amounts vary with the concentration of SWNT in the dispersion, while keeping the P123 concentration constant (Figure 4, Tables 3 and 4). The spectra of L62-NO recorded above the CMT of 1 wt % P123 in dispersions of SWNT containing 0.5, 0.75, and 1 wt % SWNT are shown in Figure 4a. The spectra clearly show that as the relative concentration of SWNT increases the relative amount of S_i increases as well. Keeping the concentration of SWNT at 1 wt % and increasing the concentration of P123 leads to an increase in the relative amount of S_m. In all
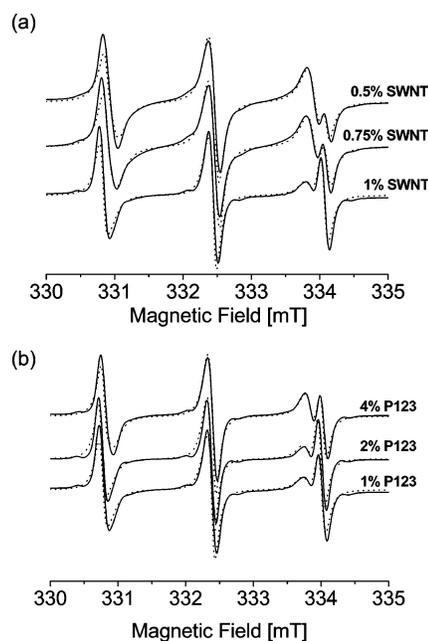

Figure 4. EPR spectra of L62-NO in SWNT dispersions in P123 at 345 K. (a) The effect of the relative SWNT concentration for a fixed concentration of P123 (1 wt %). (b) The effect of P123 concentration for a fixed concentration of SWNT of 1 wt %. Dotted lines are simulations obtained with the parameters listed in Tables 3 and 4.

cases, the values of a_{iso} and τ_c of the two species remained constant within experimental errors (Tables 3 and 4).

A similar set of experiments was carried out on dispersions of 1 wt % F127 using L62-NO as the probe. The results are shown in Figure 5. The behavior is similar to P123; while only S_m is observed above the CMT in the native solution, both S_i and S_m are observed in the SWNT dispersion. Furthermore, above the CMT, the temperature dependence of τ_c is considerably milder
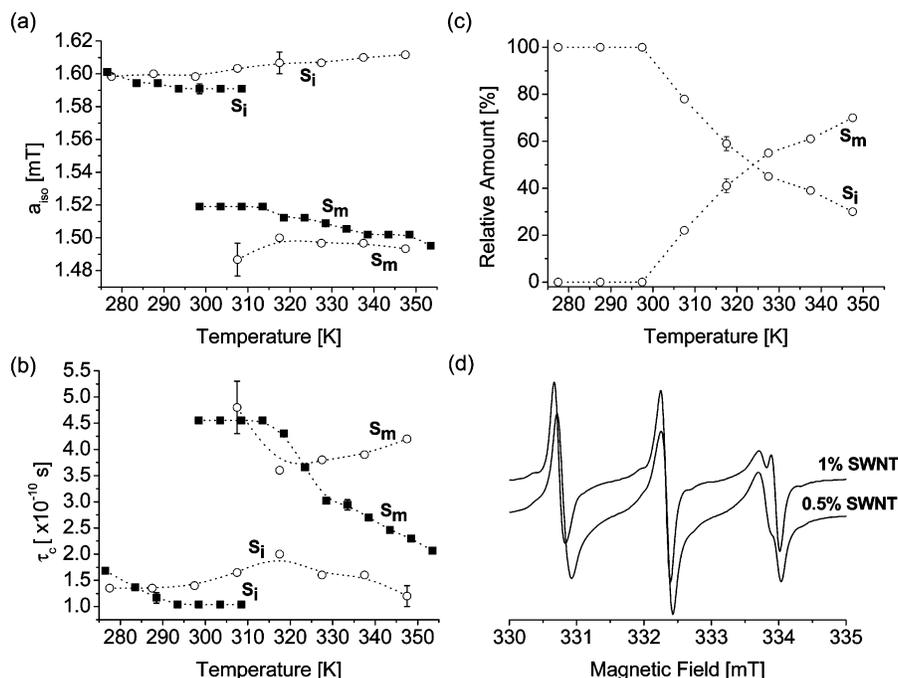
Figure 5. Temperature dependence of (a) a_{iso} and (b) τ_c of L62-NO in 1 wt % F127 solutions: (■) no SWNT; (○) dispersions of 1 wt % SWNT. (c) The relative amounts of S_i and S_m as a function of temperature of the dispersion. (d) EPR spectra of solutions with different amounts of SWNT and 1% F127.

Table 3. The Relative Amounts of S_m and S_i, a_{iso}, and τ_c of L62-NO in 1% P123 for Different Amounts of SWNT (T = 345K)

	S_m				S_i		
SWNT (wt %)	relative concn (%)	a_{iso} (mT)	τ_c ($\times 10^{-10}$ s)		relative concn (%)	a_{iso} (mT)	τ_c ($\times 10^{-10}$ s)
0.50	88 ± 2	1.48 ± 0.01	5.3 ± 0.4		12 ± 2	1.61 ± 0.01	1.1 ± 0.2
0.75	74 ± 2	1.48 ± 0.01	4.9 ± 0.4		26 ± 2	1.61 ± 0.01	1.7 ± 0.2
1	33 ± 2	1.47 ± 0.01	4.5 ± 0.4		67 ± 2	1.62 ± 0.01	1.4 ± 0.2

Table 4. The Relative Amounts of S_m and S_i, a_{iso}, and τ_c of L62-NO for Different Amounts of P123 and 1% SWNT (T = 345K)

	S_m				S_i		
P123 (wt %)	relative concn (%)	a_{iso} (mT)	τ_c ($\times 10^{-10}$ s)		relative concn (%)	a_{iso} (mT)	τ_c ($\times 10^{-10}$ s)
4	58 ± 2	1.48 ± 0.01	4.1 ± 0.4		42 ± 2	1.62 ±± 0.01	1.2 ± 0.2
2	35 ± 2	1.48 ± 0.01	4.3 ± 0.4		65 ± 2	1.62 ± 0.01	1.2 ± 0.2
1	31 ± 2	1.47 ± 0.01	4.5 ± 0.4		69 ± 2	1.62 ± 0.01	1.4 ± 0.2

Table 5. The Relative Amounts of S_m and S_i, a_{iso}, and τ_c and of L62-NO in 1% F127 for Different Amounts of SWNT (T = 345K)

	S_m				S_i		
SWNT (wt %)	relative concn (%)	a_{iso} (mT)	τ_c ($\times 10^{-10}$ s)		relative concn (%)	a_{iso} (mT)	τ_c ($\times 10^{-10}$ s)
0.50	77 ± 2	1.49 ± 0.01	5.3 ± 0.4		23 ± 2	1.59 ± 0.01	2 ± 0.2
1	46 ± 2	1.49 ± 0.01	4.0 ± 0.4		54 ± 2	1.61 ± 0.01	1.8 ± 0.2

Table 6. The Relative Amounts of S_m and S_i, a_{iso}, and τ_c of P123-NO in 1% P123 for Different Amounts of SWNT (T = 345 K)

	S_m				S_i		
SWNT wt %	relative concn (%)	a_{iso} (mT)	τ_c ($\times 10^{-10}$ s)		relative concn (%)	a_{iso} (mT)	τ_c ($\times 10^{-10}$ s)
0	100	1.50 ± 0.01	3.3 ± 0.2				
0.50	81 ± 2	1.51 ± 0.01	4.4 ± 0.4		19 ± 2	1.6 ± 0.01	1.1 ± 0.2
0.75	63 ± 2	1.51 ± 0.01	4.5 ± 0.4		37 ± 2	1.61 ± 0.01	1.6 ± 0.2
1	48 ± 3	1.51 ± 0.01	4 ± 0.5		52 ± 3	1.62 ± 0.01	1.8 ± 0.3

than in the native solution. Here, a small, but significant difference between a_{iso} of S_m in the native solution and in the dispersion is observed, showing that when the spin label is closer to the core of the micelle it can sense a more hydrophobic core in the presence of the SWNT. Here too, a decrease in the relative amount of the

SWNT leads to a decrease in the relative amount of S_i, as observed for SWNT dispersed in P123. These results are summarized in Table 5.

To complement the picture, we investigated the SA in SWNT dispersions in solutions of P123 using the P123-NO spin probe.
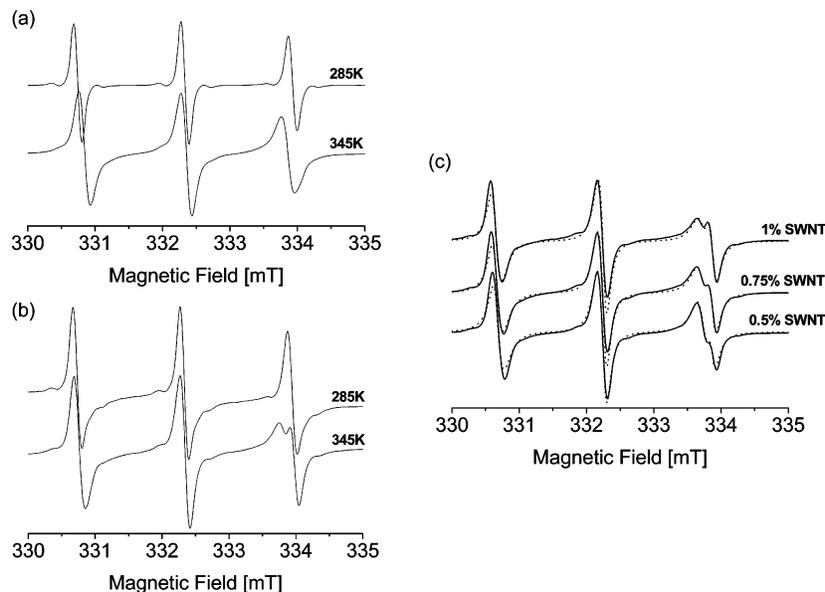
Figure 6. EPR spectra of P123-NO in solutions and dispersions of 1 wt % P123. Spectra below (285 K) and above (345 K) CMT (a) in the native solution (no SWNT) and (b) in 1 wt % SWNT dispersions. (c) Comparison of EPR spectra recorded at 345 K, above CMT, of dispersions of 0.5, 0.75, and 1 wt % SWNT in 1 wt % P123. Dotted lines are simulations obtained with the parameters listed in Table 6.
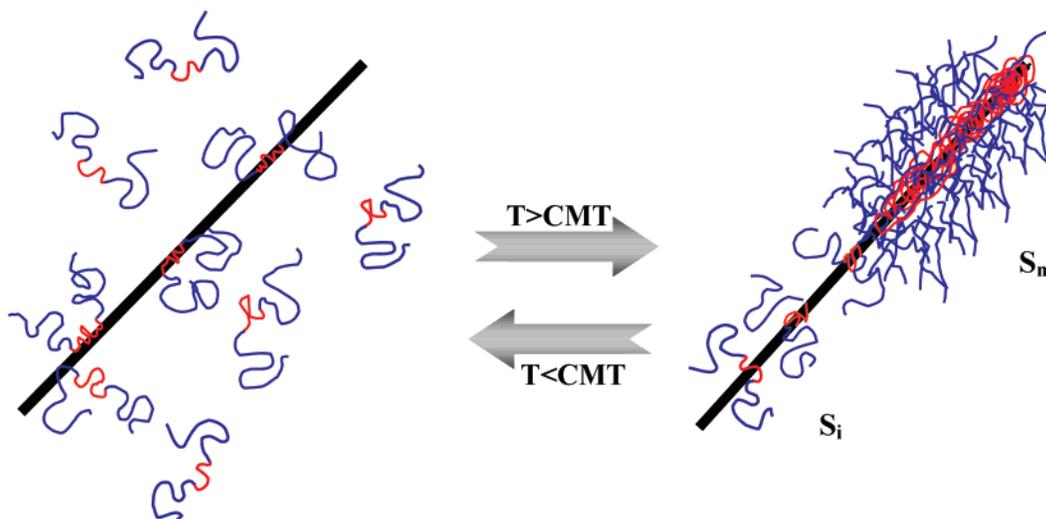

Figure 7. A schematic presenting the transition from SWNT dispersed by adsorption of Pluronic below CMT to self-assembly of Pluronics at elevated temperatures.

The latter is located in the PEO corona, closer to the water interface than L62-NO. We observed a similar behavior to that reported by the L62-NO probe. In Figure 6, we observe that in this system as well only S_i is observed below CMT both in the native solution and in the dispersion. As SA takes place, only S_m is detected in the native solution, while both S_m and S_i are present in the dispersions. The amount of S_i is substantial and increases as the relative amount of SWNT increases. The results are summarized in Table 6.

Discussion

In this study, we characterized the temperature-induced self-assembly of nonionic block copolymers in aqueous dispersions of SWNT using spin probe EPR. Two spin probes and two different block copolymers showed a similar behavior, suggesting that the observed behavior is not specific to a particular Pluronic or a spin probe. The experimental observations may be summarized as follows: at temperatures below the CMT, EPR does not distinguish between chains adsorbed on SWNT and free chains. The spin probes exhibit a_{iso} values typical of a polar

environment and a rotational correlation time, τ_c, of a free chain in solution, S_i. Thus, the PEO blocks remain highly mobile (on the EPR time scale) and solvated (hydrated). These observations are consistent with previous studies suggesting that SWNT disperse in solution through adsorption of the PPO block, causing minor alteration of the PEO moiety.[8,22] As the temperature is raised, self-assembly of chains leads to the formation of aggregates in the dispersions.[23] Above CMT, EPR data reveal substantial differences between the native polymer solution and the dispersion; while in the native solution the Pluronics spin labels experience only one environment, S_m, assigned to the corona of the Pluronic micelle, in the dispersions, we observe a second population of nonaggregated chains, S_i. The relative proportions of the two populations depend on the relative concentration of dispersed SWNT as compared to the concentration of the block copolymer. The aggregates formed in the SWNT dispersions do not show the typical increase in chain-end mobility as a func-

(22) Szleifer, I.; Yerushalmi-Rozen, R. *Polymer* **2005**, *46*, 7803−7818.
(23) We found that that SWNT modify the aggregation temperature of Pluronic block copolymers (ref 11, in press).

tion of temperature that is observed in the post-CMT regime of the native Pluronic solutions. This suggests a larger dynamical coupling among the chains within the aggregates formed in the presence of the SWNT as compared to the native micelles.

A schematic representation of the suggested picture of the SA process in the presence of SWNT is presented in Figure 7. The suggestion that aggregates formed in SWNT dispersions are composed of SWNT at the core of the aggregate is supported by the higher τ_c value of the aggregates as compared to τ_c of the (native) micellar solution and the reduced temperature dependence of τ_c in the dispersions. While the higher value of τ_c indicates the formation of aggregates with a tighter packing than those formed in the native solution, the milder temperature dependence indicates that the interaction of the block copolymers with the SWNT dominates over the temperature effect. In the scenario suggested here, free polymer micelles do not form and aggregation only takes place on the surface of the dispersed SWNT. This suggestion relies on the following argument: fast exchange on the EPR time scale between the adsorbed chains and free micelles is excluded due to the long desorption time of adsorbed polymers.[24] Thus, if two populations would exist, two distinct EPR characteristics and two CMT values should have been observed. In other words, we would expect to see two populations of S_m rather than one and a broad CMT. Our data and the DSC study[11] suggest that, within the experimental resolution, this is not the case.

The dependence of the values of the two populations (S_i, S_m) on the relative concentrations of the polymers and the SWNT is consistent with the above picture. We find that as the relative Pluronic concentration is increased S_i is reduced. This tendency is explained by the suggestion that S_i counts the population of adsorbed, nonaggregated chains. At a higher relative polymer concentration, more chains aggregate on the SWNT, leaving less single adsorbed chains, and thus S_m is higher. Following the same line of thought, when the relative amount of the SWNT is increased, we observe that S_i increases, as there are not enough Pluronic molecules to assemble on the additional SWNT now. Thus, a larger population of the adsorbed Pluronic chains remains as individual chains and contribute to S_i.

Conclusions

Using spin probe EPR, we found that SWNT affect the temperature induced self-assembly of Pluronic block copolymers in aqueous solutions, suggesting the formation of a new type of hybrid SWNT−polymer nanostructure. Detailed investigation suggested that the formation of block-copolymer micelles is suppressed while the hybrid SWNT−polymer structures dominate the system.

Supporting Information Available: Images and electron microscopy micrograph of dispersions of SWNT in Pluronic solutions as well as DSC measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

(24) Aubouy, M.; Raphael, E. *Macromolecules* **1994**, *27*, 5182−5186.

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