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"Supramolecular" Assembly of Gold Nanorods End-Terminated with Polymer "Pom-Poms": Effect of Pom-Pom Structure on the Association Modes

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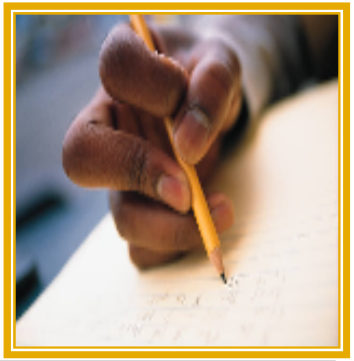

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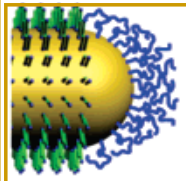


Introduction

- Because of the chemical heterogeneity the organization of nanoparticles into complex, predictable structures by the use of preferential interactions is possible.

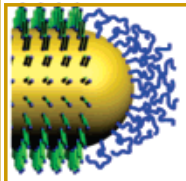
  self-assembly strategies employed conceptual similarity between multicomponent nanoparticles and their molecular analogues such as surfactants, or block copolymers

- Anisotropy brigs directionality to the assembly.
- Allows the coupling of their size- and shape-dependent optical and electronic properties, e.g., band gap, absorption, emission, and conductivity.
- Using templates and external fields
- **The tethering of inorganic NRs with organic molecules.**

Recent report

Nie, Z. H.; Fava, D.; Kumacheva, E.; Zou, S.; Walker, G. C.; Rubinstein, M. *Nat. Mater*. **2007**, *6*, 609-614.

Block copolymer approach to the self-assembly of inorganic NRs terminated with polymer molecules at both ends



The control of the self-organization of pom-pom triblock copolymers by changing their structure has not been reported

In this Paper .....

The effect of the structure of the polymer pom-poms on the organization of polymer-tethered gold NRs in the range of supramolecular structures. The structure of the polymer blocks was controlled by varying theirmolecular weight and the quality of solvent for the polymer molecules.

Experimental Methods

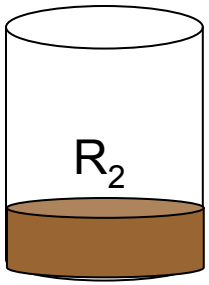
i) Preparation of Gold Nanorods (NRs)

Seed mediated growth method – El-Sayed *et.al.*

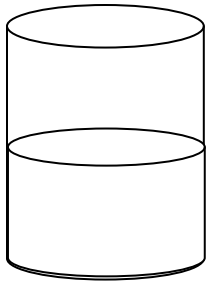
Diameter of 40 ±2 nm and 10 ± 2 nm

ii) Surface modification of gold nanorods

These will be referred to as triblocks from here on



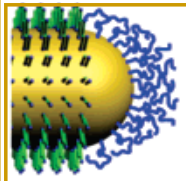
0.5 ml NR concentrated (~1.0 mg m^{-1})



10 ml of a 0.2 wt% solution of thiol-terminated polystyrene in THF

The solution was sonicated for 30 min and incubated for least 24 h.

30-min-long centrifugation cycles at 8,000 - 11,000 r.p.m. and precipitated nanorods were redispersed in DMF.



iii) Experiments of self-assembly

Drop-wise addition of water (in a mixture with DMF) to the solution of triblocks in DMF until the targeted water content was reached

iv) Estimation of the number of PS chains grafted to nanorod ends and their brush conformation

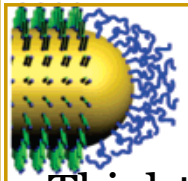
$$N_{PS} = (\rho V_{PS} N_{Av})/M_n,$$

ρ- Density of globules of polystyrene localized between the metal blocks assembled in a chain

V_{PS} - The volume of PS between adjacent self-assembled nanorods in DMF/water mixture with 20 wt% water

N_{Av} - The Avogadro number

M_n - The molecular weight of PS



Results and Discussion

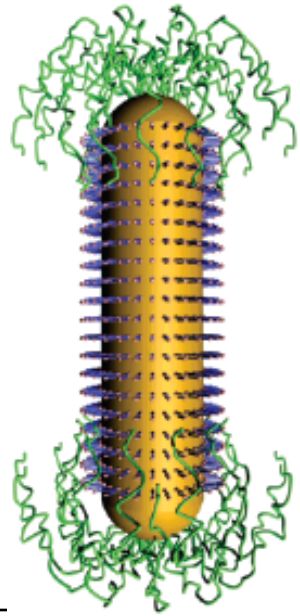
Thiol-terminated polystyrene (PSSH) molecules with the number-average molecular weights of 5000, 12 000, 20 000, 30 000, and 50 000 (referred to as PS-5K, PS-12K, PS-20K, PS-30K, and PS-50K)

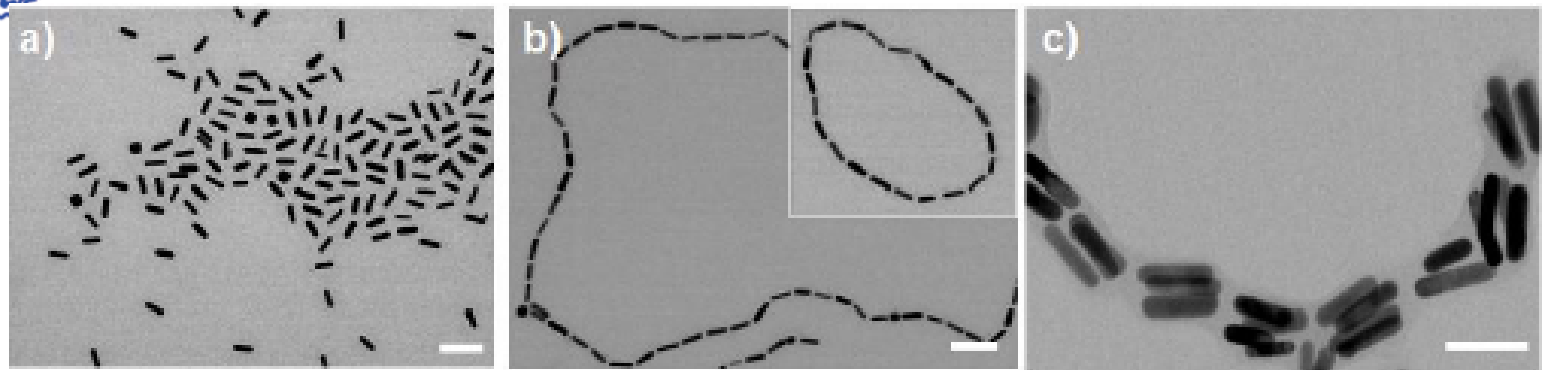
	PS-5K	PS-12K	PS-20K	PS-30K	PS-50K
N_{PS}	30	22	19	17	14

Preferential binding of CTAB along the {110} facet of the longitudinal side of the NRs left their ends (the {111} facets) deprived of CTAB and allowed for the binding of PS-SH ligands to the ends of NRs

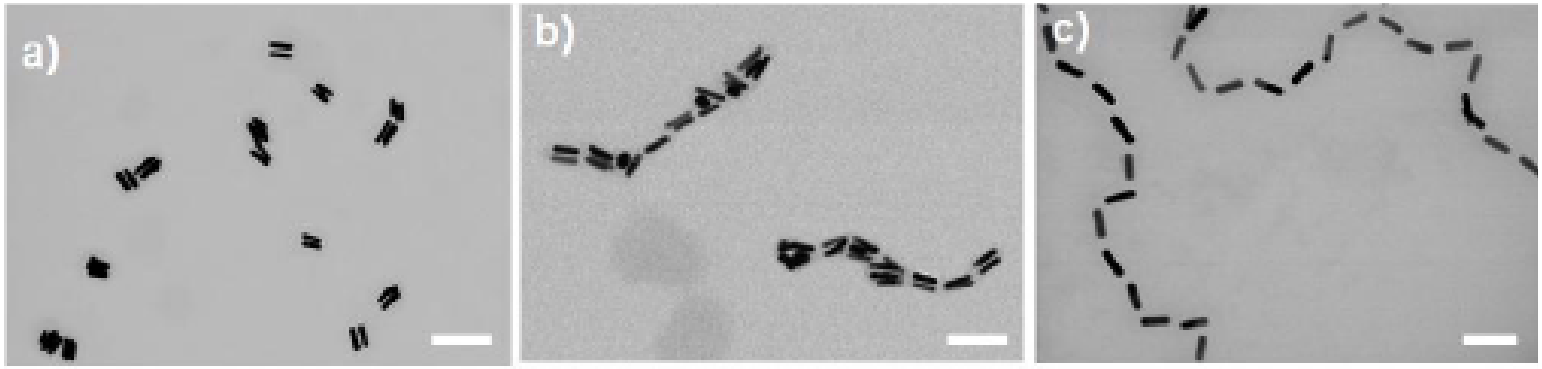
Principle of assembly

Following the addition of water, the mixture became a poor solvent for the PS blocks but remained a good solvent for the hydrophilic CTAB-stabilized metal blocks. The reducing quality of solvent for the PS constituent caused triblock association: the binding of the polymer molecules of the neighboring NRs.





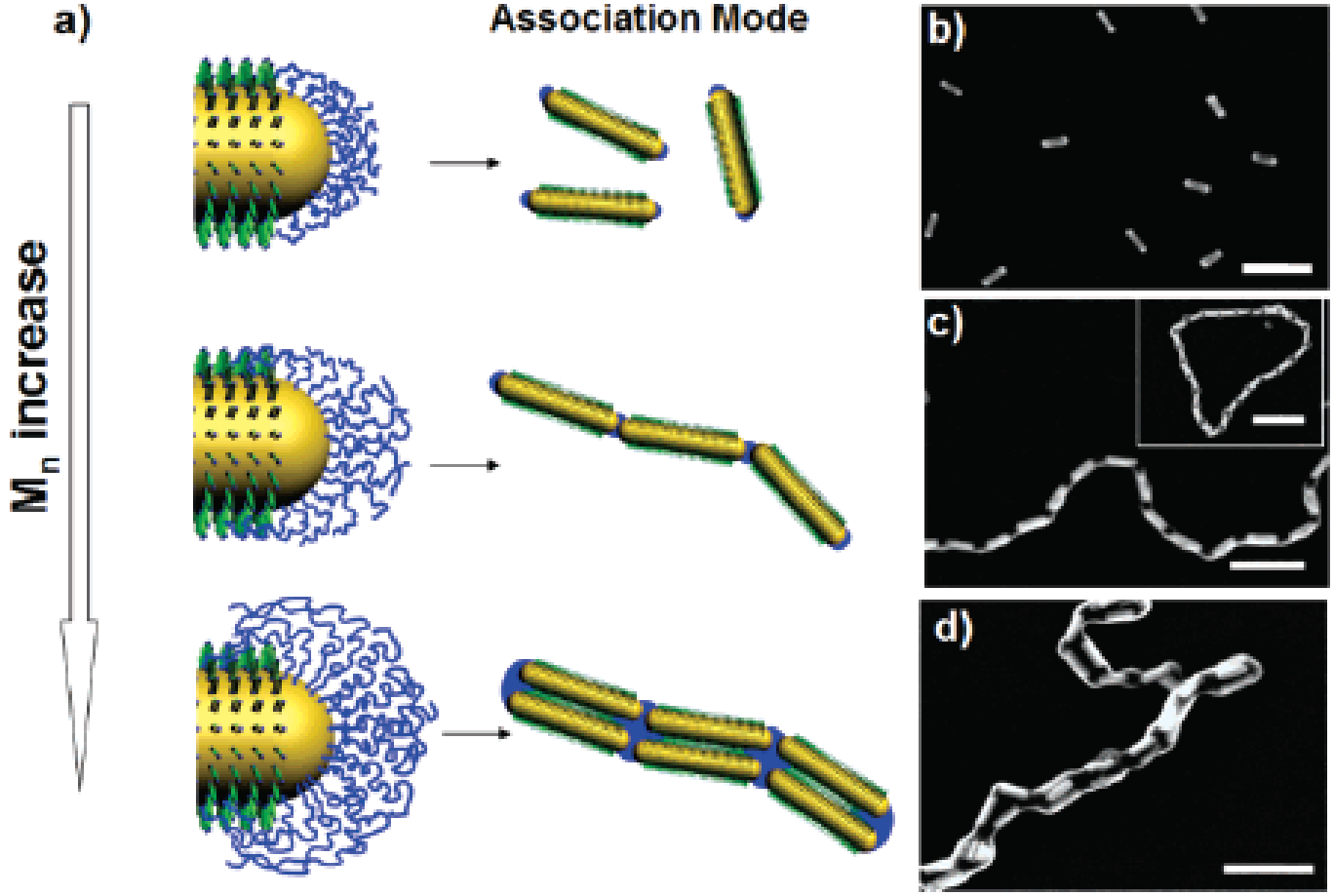
TEM images of the self-assembled structures of triblocks with varying length of triblocks: 5K-PS (a), 12K-PS (b), and 30K-PS (c) in the DMF/water mixture at CW = 6 wt%. Scale bars are 100 nm (a, b) and 50 nm (c).



TEM images of the self-assembled structures of triblocks carrying PS- 30K in the DMF-water mixtures at CW of 3 wt% (a), 6 wt% (b) and 15 wt% (c). Scale bar is 100 nm.

a) Effect of the molecular weight of PS on the self-assembly

A fixed concentration of water, C_W = 6 wt %.



Schematics of the relative location of PS molecules and SEM images of the self-assembled structures of triblocks carrying PS-5K (b), PS-12K (c), and PS-30K (d) in a water/DMF mixture with 6 wt % water. Scale bar is 100 nm.

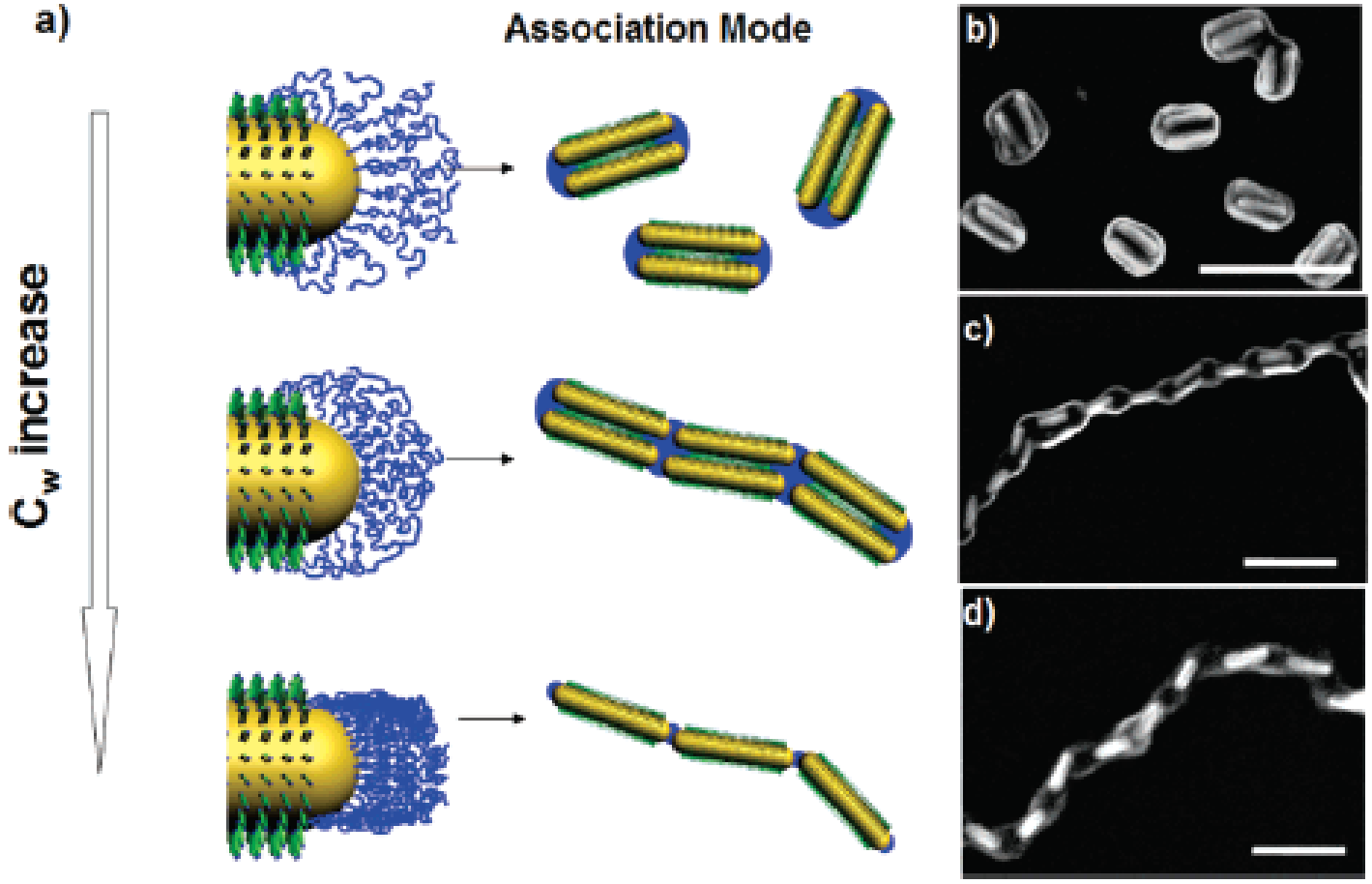
❖For short PS molecules (PS-5K) no self-assembly of triblocks occurred.

❖With increasing molecular weight of PS the triblocks organized into chains.

❖Under particular conditions (inset) the chains of triblocks formed rings.

❖Further increase in the coverage of the long side of the NR block with PS molecules led to both end-to-end and side-by-side assembly of triblocks and the formation of bundled chains.

Effect of the variation the fraction of water, CW, in the solution of NRs

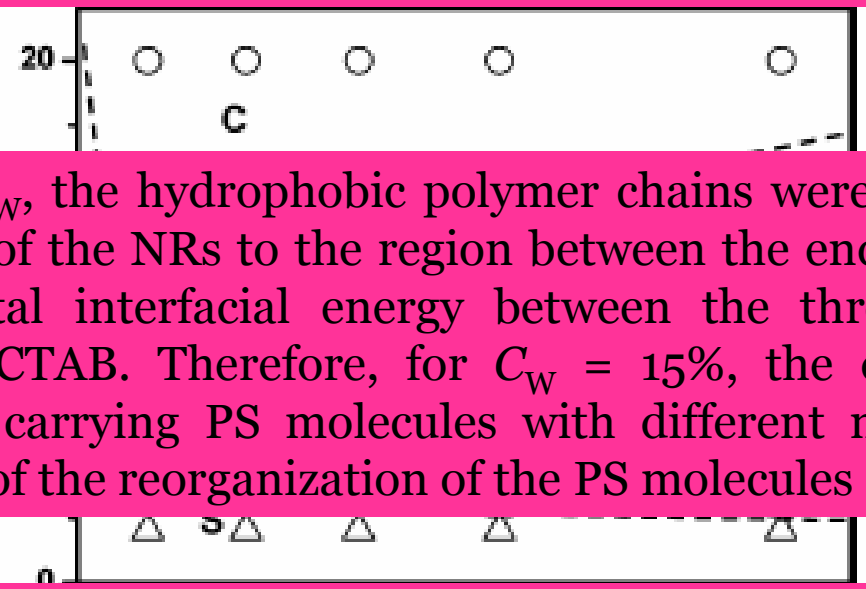


Schematics of the relative location of PS molecules and SEM images of corresponding assembled structures of triblocks with 50K-PS in water/DMF mixture with 4 wt % water (b), 10 wt % water (c), and 20 w% water (d). Scale bar is 100 nm.

For C_w < 3 wt %, the triblocks carrying PS molecules with different molecular

For 6 wt % < C_W > 8 wt %, a large fraction (up to ca. 50%) of the triblocks carrying PS-12K formed rings

The energy gain due to the linkage of PS chains of the neighboring nanorods was insufficiently high for the entropy loss due to triblock association



With increasing C_W, the hydrophobic polymer chains were pulled away from the longitudinal facet of the NRs to the region between the ends of the NRs, in order to reduce the total interfacial energy between the three phases of solvent, polystyrene, and CTAB. Therefore, for C_W = 15%, the difference in the self-assembly of NRs carrying PS molecules with different molecular weights was removed-because of the reorganization of the PS molecules

So above 15 % C_w, for all PS same assembly, ie, chains.

At the content of water of 4 wt %, the triblocks carrying PS-3K remained nonaggregated; however the triblocks comprising PS-12K assembled in the triblocks comprising PS molecules with higher molecular weights, the polymer pom-pom partly spread over the long facet of the NR block and at *CW* g6 wt % the combined side-byside and end-to-end association of triblocks yielded bundled chains

T

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30K, and PS-30K) showed preferential side-by-side assembly in bundles

Competition between the side by- side and end-to-end assembly modes of triblocks

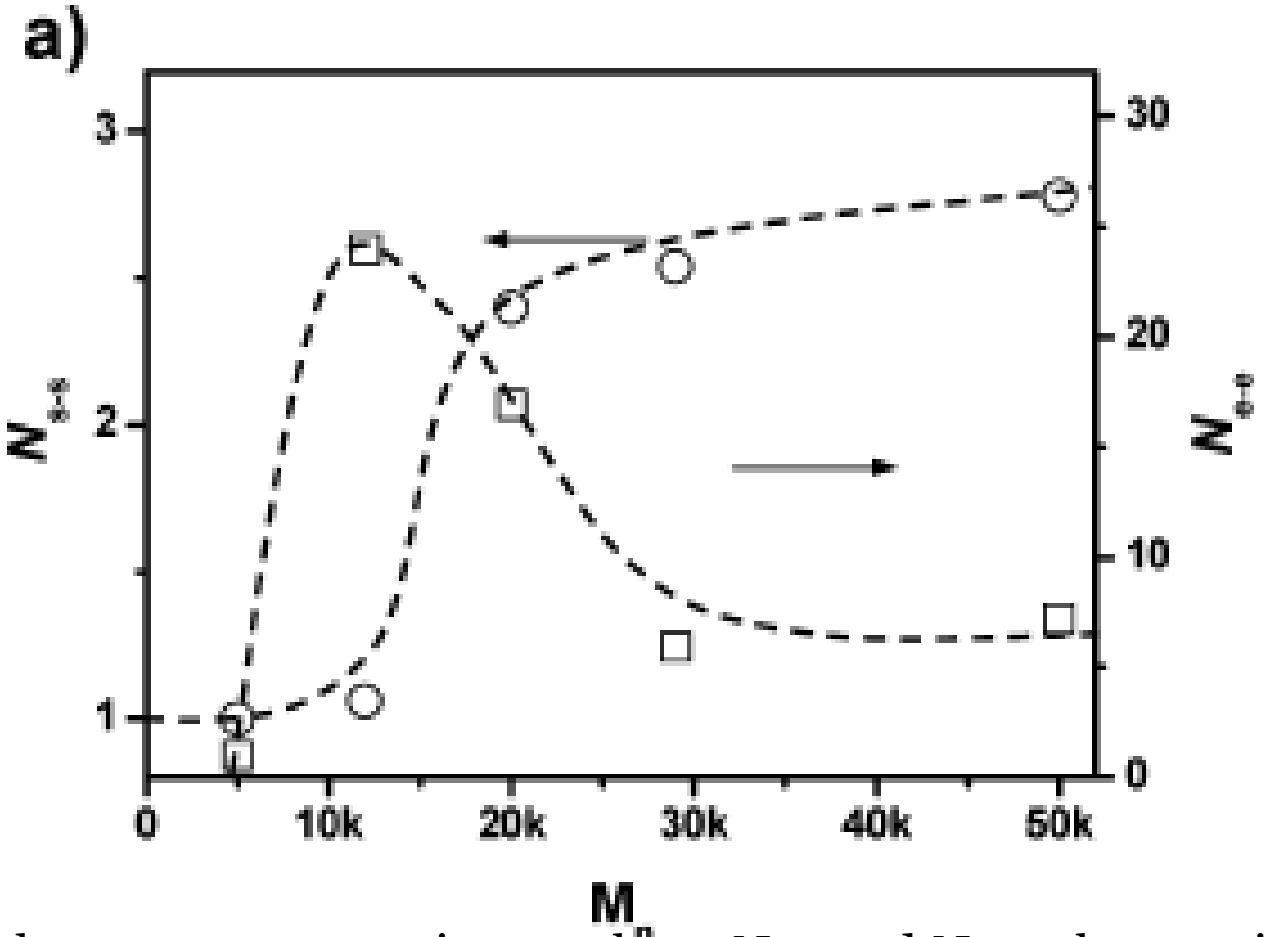
Determination of the average side-by-side and end-to-end aggregation numbers, *N*s-s and *N*e-e

$$N_{s-s} = (\sum_{i=1}^{\infty} n_i N_i / \sum_{i=1}^{\infty} n_i)$$

n_i is the number of aggregates in which N_i triblocks assembled side-by-side.

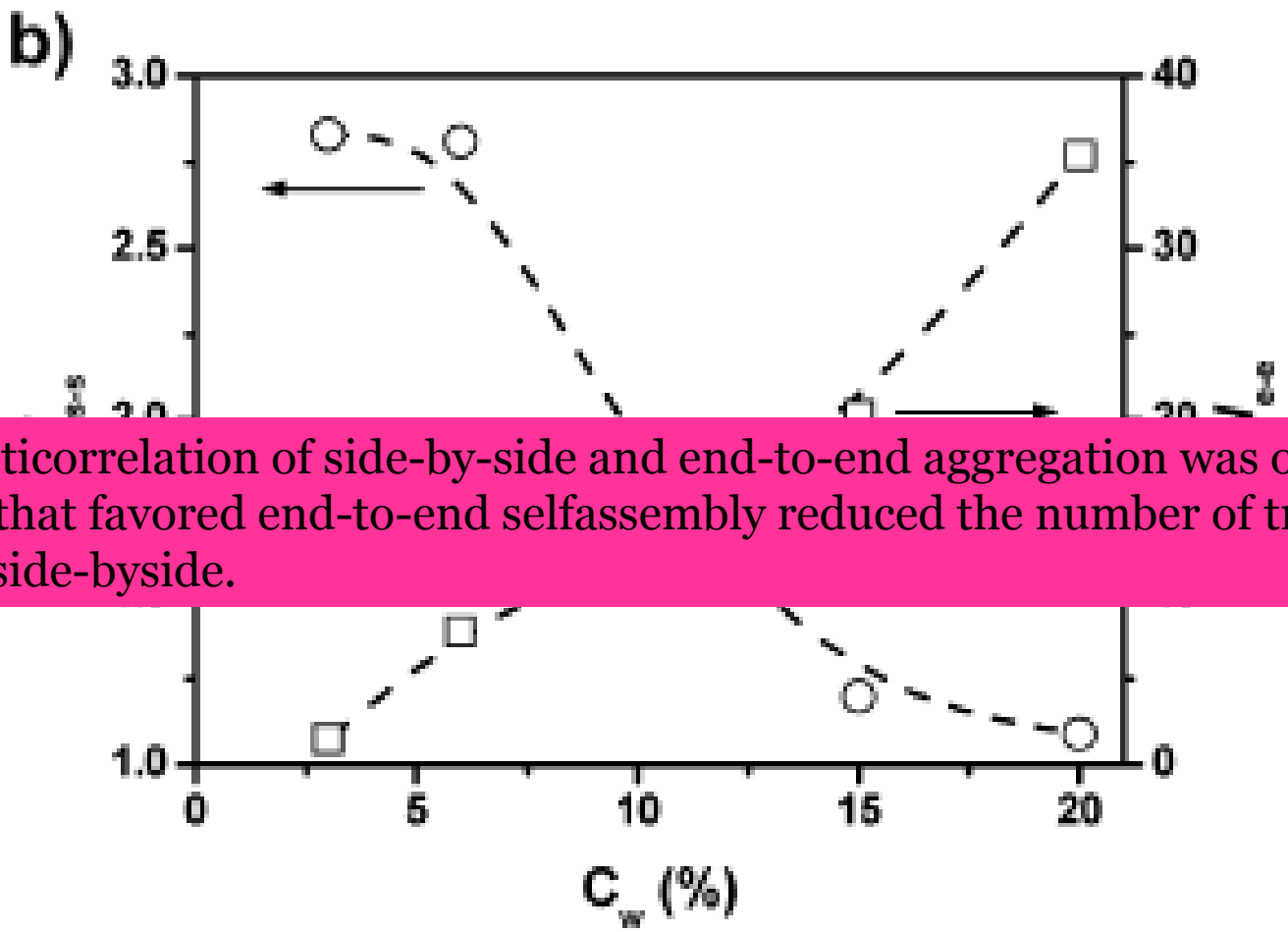
$$N_{e-e} = (\sum_{i=1}^{\infty} n_i / X)$$

X is the number of chains



Variation in the average aggregation numbers, *N*s-s and *N*e-e, characteristic for the side-by-side and end-to-end association of triblocks, respectively, plotted as a function of the molecular weight of PS in the DMF/water mixture at *C*W) 6 wt %

The value of *N*s-s increased and the value of *N*e-e decreased with the molecular weight of PS increasing from 12 000 to 50 000.



A strong anticorrelation of side-by-side and end-to-end aggregation was observed: the factors that favored end-to-end selfassembly reduced the number of triblocks associated side-byside.

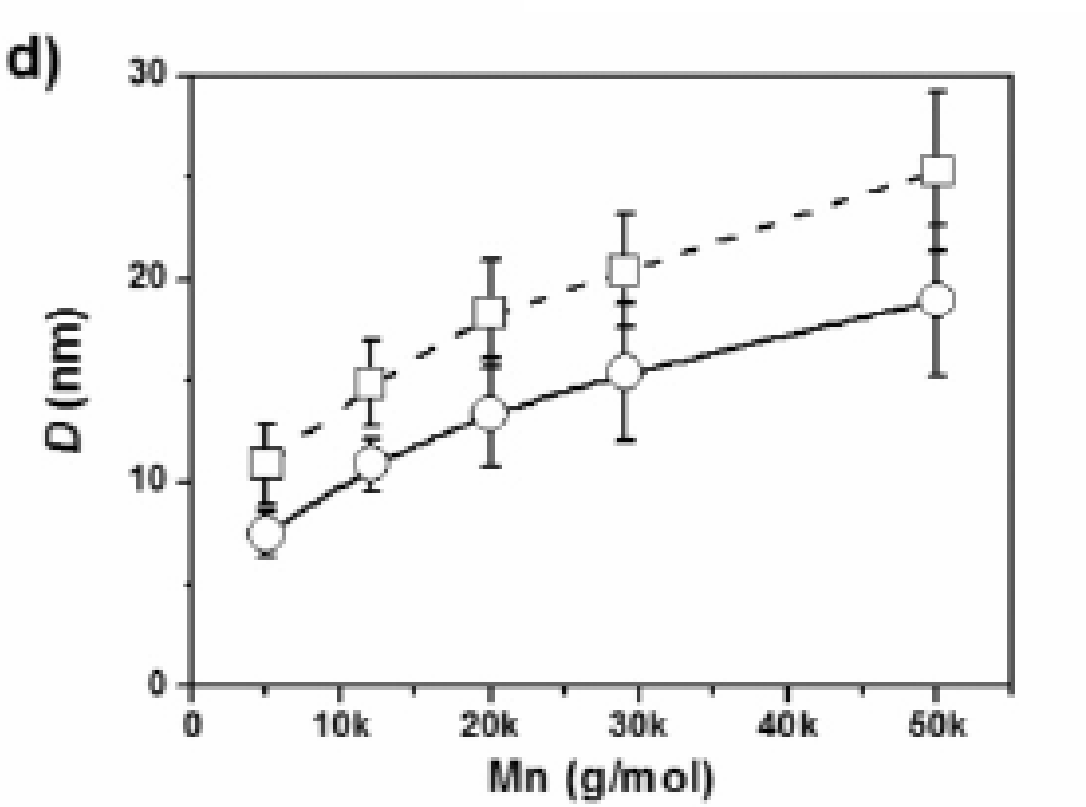
Variation in the average aggregation numbers, *N*s-s and *N*e-e, characteristic for the side-by-side and end-to-end association of triblocks, respectively, plotted as a function of the concentration of water concentration in the DMF/water

With increasing concentration of water, *N*s-s decreased from ca. 2.8 to ca. 1.1 and *N*e-e increased from ca. 2 to ca. 38

Assembly, optical spectra and distance

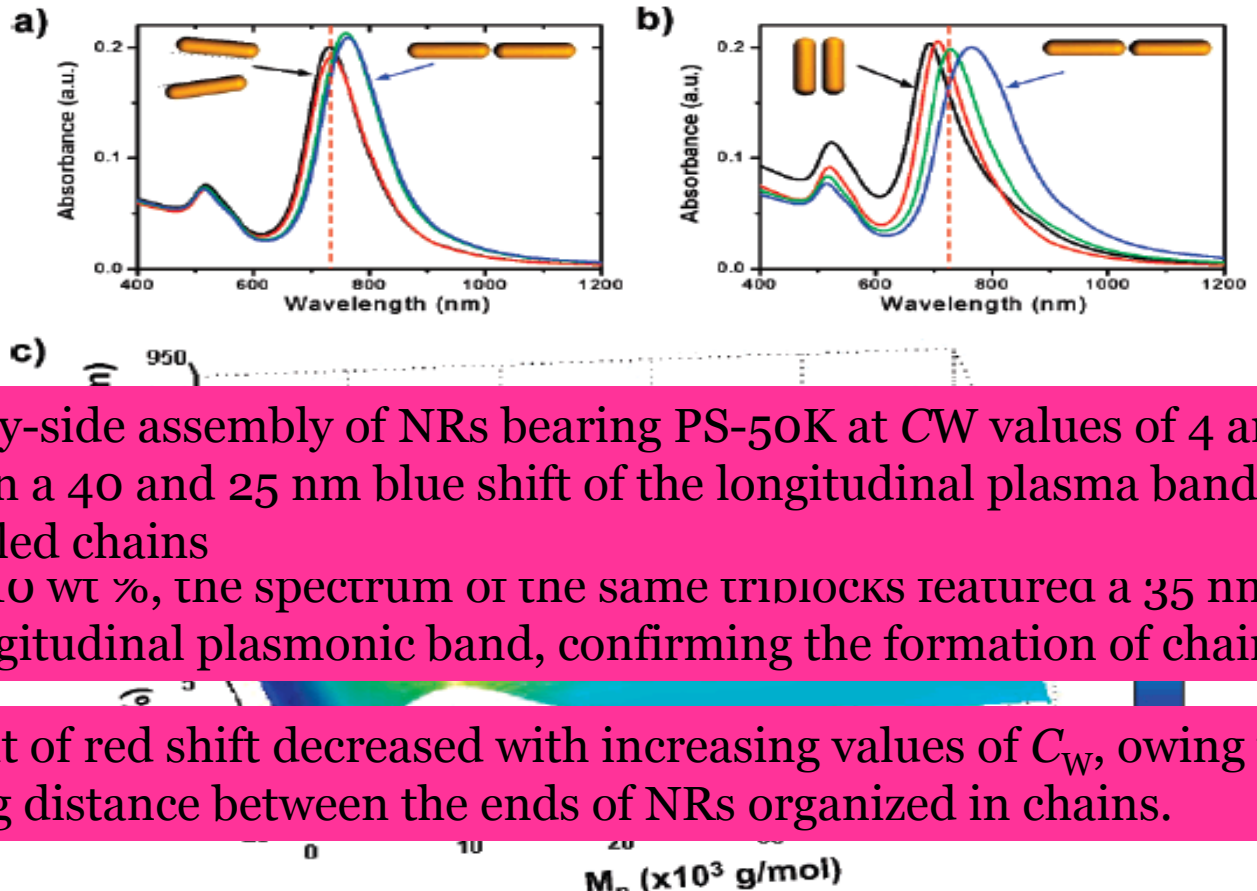
a) Effect of molecular weight of PS molecules on the distance between the ends of adjacent NRs

(a-c) TEM images of self-assembled nanochains of PS-5K (a), PS-12K (b), and PS-50K (c) in a water/DMF mixture with *C*W) 15%. Scale bar is 50 nm.



(d) Variation of the average end-to-end distance between adjacent NRs of assembled chains, *D*, at *C*W) 15% (O) and 20% (o) plotted as a function of number-average molar mass of PS.

Effect of the structure of PS pompoms on the variation in the plasmonic properties of selfassembled NRs

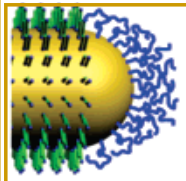


The sideby-side assembly of NRs bearing PS-50K at *C*W values of 4 and 6% resulted in a 40 and 25 nm blue shift of the longitudinal plasma band :bundles and bundled chains

At CW > 10 wt %, the spectrum of the same triblocks featured a 35 nm red shift of the longitudinal plasmonic band, confirming the formation of chains.

The extent of red shift decreased with increasing values of C_W, owing to the increasing distance between the ends of NRs organized in chains.

(a,b) UV-vis spectra of self-assembled triblocks carrying PS-5K (a) and PS-50K (b) in the DMF/water mixtures with *C*W values of 4 wt % (black), 6 wt % (red), 10 wt % (green), and 15 wt % (blue). Vertical dashed lines position of initial sample. (c) Variation in the longitudinal plasmonic bands of self-assembled nanorods plotted on the (*M*n, *C*W) space.



Conclusions

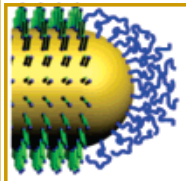
❖In the DMF/water mixtures, the self-assembly of NRs end-terminated with PS molecules originates from the pom-pom structure of the polymer blocks.

❖Assembly type is determined by the length and distribution of PS molecules between the ends of NRs and the longitudinal facet of NRs.

❖Depending on the relocation of the polymer molecules from the long facet to the end of the metal blocks, the assembly of nanorods underwent the following transitions:

bundles to bundled chains to chains

❖The transitions were controlled by two anticorrelating parameters: the molecular weight of the polymer tethered to NR ends and the concentration of water in the system.



Prospects !!!!!

Various prospects can be tried.....
Similar structures already got can be explored more.