this work provides an important advance in quantitative network theory and a foundation for further development of theories that account for interacting network defects and entanglements. Combining RENT with primary and higher-order loop measurements provides quantitative agreement with measured elastic moduli for networks with compositions and structures that are relevant to common applications. In other words, RENT can predict the bulk mechanical properties of polymer networks on the basis of molecular information. We anticipate that RENT and loop-counting methods will be applicable to a wide range of polymer networks.

REFERENCES AND NOTES

22. See supplementary materials on Science Online.

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SUPPLEMENTARY MATERIALS

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NANOMATERIALS

1D nanocrystals with precisely controlled dimensions, compositions, and architectures

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The ability to synthesize a diverse spectrum of one-dimensional (1D) nanocrystals presents an enticing prospect for exploring nanoscale size- and shape-dependent properties. Here we report a general strategy to craft a variety of plain nanorods, core-shell nanorods, and nanotubes with precisely controlled dimensions and compositions by capitalizing on functional bottlebrush-like block copolymers with well-defined structures and narrow molecular weight distributions as nanoreactors. These cylindrical unimolecular nanoreactors enable a high degree of control over the size, shape, architecture, surface chemistry, and properties of 1D nanocrystals. We demonstrate the synthesis of metallic, ferroelectric, upconversion, semiconducting, and thermoelectric 1D nanocrystals, among others, as well as combinations thereof.

Plain nanorods of varied diameters and compositions were synthesized using amphiphilic cellulose-g-(PAA-b-PS) (cellulose-graft-[poly(acrylic acid)-block-polystyrene]) BBCP nanoreactors (Fig. 1A; table S2; and supplementary text, sections III and IV). Because each unit in the cellulose backbone enables the growth of three PBrA-b-PS diblocks (upper left panel in Fig. 1A; supplementary text, sections I and II), the densely grafted PBrA-b-PS arms in conjunction with the rigidity of the backbone force the cellulose-g-(PBrA-b-PS) BBCP to adopt a straight, rigid, cylindrical conformation (upper right panel in Fig. 1A) [PBrA, poly(tert-butyl acrylate)]. Subsequent hydrolysis of the PBrA blocks yields amphiphilic cellulose-g-(PAA-b-PS) with inner hydrophilic PAA blocks and outer hydrophobic PS blocks (lower right panel in Fig. 1A and fig. S47). When cellulose-g-(PAA-b-PS) BBCPs are dispersed in dimethylformamide (DMF) polar solvent (18), the resulting unimolecular micelles can be used as nanoreactors. The interaction between highly polar DMF and the inner PAA blocks is stronger than that between DMF and the outer PS blocks. Thus, there is a greater repulsion between PAA chains in DMF than between PS chains (18). As a result, the PAA chains are greatly stretched and form a large compartment. On addition and dispersion of inorganic precursors into the solution, the cylindrical compartment containing PAA blocks can accommodate a large volume of precursors. In addition to the solvent polarity effect noted above, the precursors are also preferentially partitioned in the cylindrical PAA block compartment as a result of the strong coordination interaction between the metal moieties of precursors and the carboxylic acid groups of PAA, which creates a high enough concentration of precursors to initiate the nucleation and growth of inorganic nanorods (19) (figs. S8 to S6 and S71; see supplementary text, section IV, for the proposed formation mechanisms). The in situ capping of PS chains on the nanorods facilitates dispersion and solubility in various organic solvents (lower left panel in Fig. 1A).
As a proof of concept, we synthesized upconversion NaYF₄:Yb/Er nanorods. Transmission electron microscopy (TEM) images at different magnifications (Fig. 2A) demonstrate the formation of uniform NaYF₄:Yb/Er nanorods with an average diameter $D$ of 9.8 ± 0.5 nm and length $L$ of 97 ± 9 nm. These nanorods are highly crystalline and have a hexagonal phase, as established by high-resolution TEM (HRTEM; Fig. 2A) and x-ray powder diffraction (XRD) measurements (fig. S60). Energy-dispersive x-ray spectroscopy (EDS) confirmed the composition of the NaYF₄:Yb/Er nanorods (fig. S63). Thermogravimetric analysis (TGA) showed that the volume percentage of PAA blocks encapsulated by NaYF₄:Yb/Er nanorods was ~11.2% (fig. S54).

As a living free-radical polymerization technique, ATRP affords excellent molecular weight (MW) control (20), enabling the precise design of BBCPs with a tunable MW and narrow MW distribution for each constituent block (table S2 to S10). Consequently, the diameter of 1D plain nanorods is dictated by the length of the hydrophilic inner block in BBCPs, which can be regulated by tuning the polymerization time of the different blocks during ATRP. Moreover, the solubility of 1D nanocrystals (organic solvent–soluble or water-soluble) is rendered by the outer blocks of the BBCP brushes, which are covalently bonded to the inner blocks. Lastly, the length of 1D nanocrystals can be adjusted by varying the length of the macroinitiator (denoted cellulose-Br; supplementary text, section I).

To obtain a specific length of cellulose-Br macroinitiator, natural cellulose modified with 2-bromoisobutyryl bromide in a mixed solvent of ionic liquid, anhydrous 1-methyl-2-pyrrolidione (NMP), and DMF was purified by fractional precipitation (figs. S1 to S3; table S1; and supplementary text, section I). Taking noble metallic Au nanorods as an example, facile control over the nanorod length and diameter was achieved by deliberately tuning the length of the cellulose-Br macroinitiator and the MW of the PAA blocks, respectively, in cellulose-g-(PAA-b-PS) (Fig. 2B). As the MW of cellulose-Br increased from $11.2 \times 10^3$ to 79.6 × $10^3$ g/mol, the length of the Au nanorods increased from 51 ± 4 to 434 ± 39 nm. By increasing the MW of the PAA block from $5.2 \times 10^3$ to $11.2 \times 10^3$ g/mol, the diameter of the Au nanorods increased from 10.4 ± 0.6 to 21.2 ± 1.5 nm.

Conceptually, because many appropriate precursors are amenable to the cylindrical unimolecular nanoreactor strategy, a variety of uniform nanorods can be created. Figure 3 shows noble metallic Au (figs. S12, S55, and S66) and Pt (fig. S13), ferroelectric BaTiO₃ (fig. S18), upconversion NaYF₄:Yb/Er (figs. S14, S15, and S58) and NaYF₄:Yb/Tm (figs. S16, S17, and S59), semiconducting CdSe (figs. S19 and S57), thermoelectric PbTe (figs. S20 and S67), and magnetic Fe₃O₄ (fig. S21) nanorods synthesized by our cylindrical cellulose-g-(PAA-b-PS) nanoreactor approach. The possible mechanisms for the growth of these plain nanorods are shown in figs. S38 to S42 (supplementary text, section IV). Their crystalline lattices are shown as insets in Fig. 3 and fig. S52, with their crystal structures and compositions substantiated by XRD (fig. S60) and EDS measurements (fig. S63) (supplementary text, section IX). Because the nanorods are capped with PS chains that prevent their aggregation (figs. S48 to S50), they are homogeneously soluble in a wide range of organic solvents (e.g., toluene and chloroform) (fig. S53). The excess precursors that are present outside the cylindrical BBCP nanoreactor can easily form large, irregular, inorganic materials because of the lack of surface capping by PS chains, and thus they readily precipitate from organic solvents when subjected to low-speed centrifugation. Alternatively, the upper solution containing the 1D nanocrystals can also be directly retrieved. Our nanoreactor strategy is effective in producing relatively pure 1D nanocrystals (figs. S51 and S70 and supplementary text, section V).

A double-hydrophilic cylindrical cellulose-g-(PAA-b-PEG) BBCP was synthesized by a combination of ATRP and a click reaction (fig. S9; table S3; and supplementary text, section II) (PEG, poly(ethylene glycol)). Using this as a nanoreactor, we created a series of water-soluble PEG-capped
Fig. 2. Formation of plain nanorods. (A) TEM images of upconversion NaYF₄:Yb/Er nanorods templated by cellulose-g-(PAA-b-PS) (sample 2A in table S2). The lower right panel is a HRTEM image showing crystal lattices. The insets are digital images of NaYF₄:Yb/Er nanorods in toluene (lower left panel) and dry state (upper right panel) before (left) and after (right) exposure to a 980-nm near-infrared laser. (B) The dimensional tunability of 1D Au nanorods is shown as an example. The upper panel shows the dependence of the length $L$ of Au nanorods on the molecular weight $M_N$ of cellulose-Br macroinitiator (table S1). The lower panel shows the dependence of the diameter $D$ of Au nanorods (marked by arrows in the insets) on the molecular weight of PAA block in BBCP (table S2).

Fig. 3. TEM images of a variety of plain nanorods templated by cellulose-g-(PAA-b-PS). The dimensions of these nanorods are as follows: noble metallic Au, $L = 206 \pm 19$ nm and $D = 21.2 \pm 1.5$ nm from sample 3B; noble metallic Pt, $L = 48 \pm 5$ nm and $D = 10.2 \pm 0.6$ nm from sample 1A; ferroelectric BaTiO₃, $L = 101 \pm 8$ nm and $D = 106 \pm 0.8$ nm from sample 2A; upconversion NaYF₄:Yb/Er (green-emitting), $L = 99 \pm 10$ nm and $D = 9.6 \pm 0.4$ nm from sample 2A; upconversion NaYF₄:Yb/Tm (blue-emitting), $L = 103 \pm 7$ nm and $D = 10.4 \pm 0.5$ nm from sample 2A; semiconducting CdSe, $L = 98 \pm 9$ nm and $D = 10.1 \pm 0.7$ nm from sample 2A; thermoelectric PbTe, $L = 102 \pm 10$ nm and $D = 9.9 \pm 0.6$ nm from sample 2B; magnetic Fe₃O₄, $L = 203 \pm 16$ nm and $D = 10.2 \pm 0.8$ nm from sample 3A and $L = 916 \pm 87$ nm and $D = 10.3 \pm 0.5$ nm from sample 5A. Insets at the bottom of each panel are HRTEM images showing the crystal lattice of the sample. The upper insets in the middle-left and center panels are digital images of green-emitting NaYF₄:Yb/Er and blue-emitting NaYF₄:Yb/Tm nanorods, respectively, under near-infrared laser illumination (980 nm at 2 W). The upper insets in the bottom right panel are digital images demonstrating the magnetic properties of Fe₃O₄ nanorods as they were deposited on the wall of vial (right) by a magnetic bar. Further details about the samples are given in table S2.
plain Au (figs. S22, S23, and S66), NaYF4:Yb/Er (fig. S24), and Fe3O4 (fig. S25) nanorods (supplementary text, section III). These water-soluble ID nanocrystals are pertinent to a number of scientific areas, including self-assembly, bioimaging, and biosensors.

Our cylindrical BBCP nanoreactor strategy also affords a platform to synthesize high-quality core-shell nanorods composed of two different materials that have large lattice mismatches. For the synthesis of high-quality core-shell nanoparticles, a moderate lattice mismatch (<2%) between two dissimilar materials is necessary for successful epitaxial growth (22). This greatly limits the core and shell material choices for sequential epitaxial growth (22). Furthermore, in comparison with core-shell nanoparticles, the effective methods to produce core-shell nanorods are few and limited in scope (23).

The creation of core-shell nanorods with controlled dimensions (core diameter, shell thickness, and length), compositions, and solubility is enabled by using a class of cylindrical BBCPs comprising densely grafted amphiphilic triblock copolymer side chains. Specifically, cellulose-g-(P4VP-b-PtBA-b-PS) and cellulose-g-(P4VP-b-PtBA-b-PEG) can serve as organic-soluble and water-soluble nanoreactors, respectively (supplementary text, section III) [PV4P, poly(4-vinylpyridine)]. Similar to the synthesis of plain nanorods, in polar DMF solvent, precursors are selectively partitioned in the corresponding template compartments of the triblock copolymer-containing BBCPs by means of a favorable coordination interaction between the functional groups of the template blocks and the metal moieties of the precursors. In succession, the core and shell components of the nanorod can be grown.

We describe the synthesis of nanorods with a noble metallic Au core and a magnetic Fe3O4 shell as an example to demonstrate the effectiveness of cylindrical cellulose-g-(P4VP-b-PtBA-b-PS) BBCPs (upper right panel in fig. 1B) as nanoreactors in producing organic solvent-soluble core-shell nanorods (supplementary text, section III). The Au core nanorod with \( L = 103 \pm 7 \text{ nm} \) and \( D = 10.5 \pm 0.6 \text{ nm} \) (fig. 4A and fig. S68) was synthesized in DMF through preferential partitioning of Au precursors in the compartment of the inner P4VP blocks, whose pyr gyl groups imparted and coordinated with a large population of precursors (central panel in fig. 1B). The possible formation mechanism is illustrated in fig. S43. Subsequently, the PtBA blocks of the PtBA-b-PS capping on the surface of the Au-core nanorods were hydrolyzed into PAA blocks (supplementary text, section III), thus templating the formation of the Fe3O4 shell in DMF in a similar fashion to that of the Au core (fig. S44). The resulting Au-Fe3O4 core-shell nanorods capped by PAA exhibited uniform dimensions. The HRTEM image clearly shows the dark crystalline Au core surrounded by a shell of relatively lighter Fe3O4 (4.6 ± 0.4 nm thick) (fig. 4B). The XRD and EDS measurements further verified the crystal structure and composition of Fe3O4 and Au, respectively (figs. S61 and S64). It is important to note that despite a lattice mismatch of more than 50% between Fe3O4 and Au (24), Au-Fe3O4 core-shell nanorods were successfully created by capitalizing on the cylindrical cellulose-g-(P4VP-b-PtBA-b-PS) BBCP nanoreactor. Many other material combinations can also be prepared to produce organic solvent-soluble core-shell nanorods (e.g., magnetic-metallic Fe3O4-Au, shown in fig. S26, and metallic-semiconducting Au-TiO2, shown in figs. S27, S28, and S45). Similarly, the use of the cylindrical cellulose-g-(P4VP-b-PtBA-b-PEG) BBCP (supplementary text, section III; upper right panel in fig. S10) as a nanoreactor yielded water-soluble core-shell nanorods (lower left panel in fig. S10), such as metallic-semiconducting Au-TiO2 (figs. S29 and S30) and metallic-upconversion Au-NaYF4:Yb/Er (fig. S31), each with hydrophilic PEG blocks directly tethered to their surface (table S5 and supplementary text, section III). Likewise, the crystal structures and compositions of these nanorods were confirmed by XRD and EDS measurements (supplementary text, section IX).

The core diameter and shell thickness of nanorods can be precisely tuned by varying the MW of the inner P4VP block and the intermediate PtBA block. These are controlled by mediating the sequential ATRP polymerization times. A uniform nanorod length is attained by controlling the length of the cellulose-Br macroinitiator through fractional precipitation. Because the core and shell materials can be grown independently in their respective templates, the lattice structure of the synthesized shell material can be completely independent of the core material. This cylindrical BBCP nanoreactor strategy can virtually eliminate the restriction on lattice matching requirements (27). Thus, our cylindrical BBCP composed of amphiphilic triblock copolymer arms can be used to create a new class of exotic core-shell nanorods that would otherwise be challenging to obtain. Through the precise tailoring of various core and shell combinations, it is possible to explore potentially new coupled size- and shape-dependent properties.

The amphiphilic cylindrical BBCP nanoreactor strategy can also be used to synthesize uniform nanotubes (hollow nanorods) by selectively
restricting the appropriate precursors to the intermediate B block of an A-B-B-b-A BBCP tri-block copolymer nanoreactor. The inside and outside surfaces of the nanotubes are capped by inner and outer A blocks. As an example, organic solvent-soluble Au nanotubes (table S6 and supplementary text, section III) were synthesized by using amphiphilic cellulose-g-(PS-b-PAA-b-PS) as a nanoreactor (upper right panel in Fig. 1C and fig. S69). The Au precursors were sequestered in the compartment containing the intermediate PAA blocks and ultimately formed PS-capped Au nanotubes (lower left panel in Fig. 1C). In Fig. 4C, the center of the nanotubes appears brighter, signifying that they are hollow. The HRTEM image (lower right panel in Fig. 4C) and XRD pattern (fig. S62) suggest that the nanotubes are highly crystalline. Moreover, EDS measurements further corroborate the successful formation of Au nanotubes (fig. S65). The diameter of the hollow interior and the thickness of the nanotube can be controlled by tailoring the MWs of the inner PS block and intermediate PAA block during sequential ATRP. Thus, an assortment of nanotubes with different sizes and compositions can be produced, including upconversion NaYF₄:Yb/Er nanotubes (figs. S32 and S33) and semiconductor TiO₂ nanotubes (figs. S34 and S46). Despite the uniform diameter and thickness, there was a distribution of Au nanotube lengths (Fig. 4C) because of the different lengths of the individual cellulose-Br macroinitiators used to prepare the cellulose-g-(PS-b-PAA-b-PS) nanoreactors. However, cellulose-Br macroinitiators with uniform lengths can be realized by fractional precipitation. Likewise, by using cellulose-g-(PS-b-PAA-b-PEG) nanoreactors (fig. S1I), water-soluble nanotubes (e.g., Au, TiO₂, and NaYF₄:Yb/Er) nanotubes in figs. S35, S36, and S37, respectively) can also be synthesized (table S7 and supplementary text, section III).

All of the 1D nanocrystals that we produced (Figs. 2 to 4) had round ends. This is not surprising, given that each cellulose backbone was heavily grafted with diblock or triblock copolymer arms. These arms can stretch out at the two ends of the cylindrical BBCPs because of the available space there. Moreover, the two ends of the cellulose backbone have two hydroxyl groups, which allows for the growth of a diblock or triblock copolymer arm at each end. Together, the brushes on the ends of the cylindrical BBCPs have a hemispherical chain conformation. This leads to the formation of hemispherical-shaped nanocrystals situated at both ends of the 1D nanocrystals. The reaction temperature for the synthesis of nanorods was lower than the degradation temperature Tₙₜ of nanoreactors measured by TGA [e.g., Tₙₜ = 210°C for cellulose-g-(PPA-b-PS)] (fig. S44). Thus, the polymer templates are likely encased by 1D nanocrystals.

We have developed a general and robust strategy for the synthesis of a variety of 1D nanocrystals in a way that allows high-level control over dimension, anisotropy, composition, surface chemistry, and architecture. Central to this effective strategy is the rational design and synthesis of functional BBCPs—composed of a cellulose backbone densely grafted with diblock or triblock copolymers of precisely tunable lengths—that serve as nanoreactors. All of these 1D nanocrystals can be used as building blocks in the bottom-up assembly of nanostructured materials and devices with desirable characteristics (enabled by the properties of individual nanocrystals and their proper spatial arrangement) for use in optics, electronics, optoelectronics, magnetic technologies, sensors, and catalysis, among other applications. They can also serve as model systems for fundamental research in self-assembly, phase behavior, and crystallization kinetics of nanocrystals (26).

REFERENCES AND NOTES


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SUPPLEMENTARY MATERIALS

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MARINE MICROBIOME

Decoupling function and taxonomy in the global ocean microbiome

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Microbial metabolism powers biogeochemical cycling in Earth’s ecosystems. The taxonomic composition of microbial communities varies substantially between environments, but the ecological causes of this variation remain largely unknown. We analyzed taxonomic and functional community profiles to determine the factors that shape marine bacterial and archaeal communities across the global ocean. By classifying >30,000 marine microorganisms into metabolic functional groups, we were able to disentangle functional from taxonomic community variation. We find that environmental conditions strongly influence the distribution of functional groups in marine microbial communities by shaping metabolic niches, but only weakly influence taxonomic composition within individual functional groups. Hence, functional structure and composition within functional groups constitute independent and roughly equally weighted “axes of variation” shaped by markedly different processes.

Microbial communities drive global biogeochemical cycling (7). Bacteria and archaea, for example, strongly influence marine carbon, nitrogen, and sulfur fluxes, thereby modulating global ocean productivity and climate (2, 3). Elucidating the processes that shape microbial communities over space and time is important for predicting how biogeochemical cycles will change with changing environmental conditions.

Taxonomic microbial community profiling can reveal intriguing, but often unexplained, variation

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