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Surfactant-Assisted Elimination of a High Energy Facet as a Means of Controlling the Shapes of TiO₂ Nanocrystals

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Abstract: The surfactant-mediated shape evolution of titanium dioxide anatase nanocrystals in nonaqueous media was studied. The shape evolves from bullet and diamond structures to rods and branched rods. The modulation of surface energies of the different crystallographic faces through the use of a surface selective surfactant is the key parameter for the shape control.

Introduction

The synthesis of inorganic nanocrystals with controlled shape, potential materials with directional and shape dependent properties, is an important goal of advanced materials chemistry. Many reports have described the shape controlled synthesis of anisotropic inorganic nanocrystals in liquid media,^{1–3} one general approach being the growth of nanocrystals in the presence of surfactants that selectively bind to specific crystalline facets.^{4–11} This method relies on the fact that faceted rather than spherical seeds are nucleated and the different facets are characterized by different surface energies. Crystal growth rates are in turn exponentially correlated to the crystal surface energy, and therefore anisotropic nanocrystal growth can result by enhancing or reducing the surface energy by surfactant adhesion.

We have successfully applied this approach to chalcogenide semiconductors^{4–8} and metal⁹ colloid synthesis. In the case of hexagonally structured cadmium selenide,^{4,5} rod shaped nanocrystals are obtained by growing the nanoparticles in the presence of alkylphosphonic acids. The rods are elongated along the [001] direction as a consequence of the selective adhesion of alkylphosphonic acids on the other directions.⁴ Disk shaped Co nanocrystals⁹ can be formed as a result of strong adhesion

of alkylamines on {001} facets, which hinders their growth. Recently, it has been proven that anisotropic shapes can be obtained even in highly symmetric crystal structures by enhancing differences in growth rates of different facets. In the cubic PbS system,⁸ selective adhesion of thiol molecules onto the {111} faces results in fast growth along the <100> directions, producing cross- and star-shaped particles.

Studies on nanocrystal shape evolution, however, have mostly been focused on specific materials and crystal shapes, limiting the general understanding of the nanocrystal shape evolution process and the possibility to exploit their growth mechanisms for other materials and geometries. In particular, until now the use of selective surfactants has been mainly limited to the production of anisotropic shapes arising from blocking or retarding the growth along one or more directions by selective adhesion. A more interesting prospective application of surface-selective surfactants would be to finely tune the growth rate of the faces to follow the resulting shape evolution process. In general, highest energy facets are eliminated during crystal growth; thus, progressive addition of a selective surfactant should yield a sequence of shapes.

We address this issue by presenting the study of the shape evolution process of titanium dioxide anatase nanocrystals via surface energy control in the kinetic growth regime.

TiO₂ anatase has a tetragonal structure (the *c*-axis being 2.7 times the *a*-axis) and has been shown to nucleate as truncated octagonal bipyramid seeds,¹² exposing eight equivalent {101} faces and two equivalent {001} faces. According to Donnay–Harker rules,¹³ the surface free energy of the {001} faces is ~1.4 times larger than that for the {101} faces. As these features determine an intrinsic instability of the nucleus, the TiO₂ anatase offers an interesting case to study shape evolution in terms of relationship between surface free energy and growth rate. Moreover, the symmetry of the anatase structure allows one to

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see whether the equivalent faces will follow the same fate during crystal growth, as expected.

Carboxylic acids bind very strongly to anatase 001 facets, being still absorbed at temperatures as high as 750 K, as detected by temperature programmed desorption and STM observations.¹⁴ On the basis of these results, the presence of surface-selective surfactants such as carboxylic acids in anatase crystallization may affect the outcome in the resulting crystal shape.

In this paper, we vary the ratio of a nonselective and a surface selective surfactant, which act upon the intrinsic anisotropic features of anatase, to induce the shape evolution of TiO₂ nanocrystals from bullet and diamond to rod and branched shapes. We use lauric acid (LA, CH₃(CH₂)₁₀COOH) as the selective surfactant and trioctylphosphine oxide (TOPO, [CH₃(CH₂)₇]₃PO) as the nonselective surfactant.

Experimental Section

General Methods. All procedures were carried out using standard airless techniques under argon. All chemicals were purchased from Aldrich. Trioctylphosphine oxide (TOPO) and lauric acid were dried and degassed by heating at 100 °C for an hour before use.

Synthesis of TiO₂ Nanocrystals. The synthesis of TiO₂ nanocrystals with various shapes was accomplished by an alkyl halide elimination reaction between titanium chloride and titanium isopropoxide.¹⁵ Typically, TiO₂ nanocrystals were synthesized by the following procedure. A dioctyl ether solution (Oc₂O, 5.00 g) containing trioctylphosphine oxide (TOPO) and lauric acid (LA) was heated to 300 °C followed by addition of 2.0 mmol of titanium chloride under vigorous stirring. The reaction was initiated by the rapid injection of 2.0 mmol of titanium tetraisopropoxide (TTIO) into the hot solution. After 10–20 min, the resulting solution was quenched with cold toluene and treated with acetone to precipitate white flocculates that were subsequently separated by centrifugation. The white powders obtained were washed twice with acetone and redissolved in toluene.

The relative ratio between TOPO and lauric acid was varied while keeping the total amount of surfactant molecules to 20.6 mmol. For the low LA concentration experiment, 2.0 mmol of LA and 18.6 mmol of TOPO were used. For the medium LA concentration experiments, 4.0 mmol of LA and 16.6 mmol of TOPO were used. In the high and excess LA concentration experiments, 8.0 and 16.0 mmol of LA were used, respectively.

Growth Kinetics Experiments. All growth kinetics experiments were performed in a solution containing 8.0 mmol of LA and 12.8 mmol of TOPO in 5.00 g of Oc₂O at 300 °C. Aliquots (~0.5 mL) were removed from the solution at 1, 2, 4, 8, 15, and 40 min after precursor injection and quenched with a small amount of toluene. For the ripening experiment, growth times at 300 °C of 1 and 2 days were adopted. The products were washed through repeating redissolving and precipitation processes with toluene and acetone, respectively.

Characterization. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) observations were carried out on a Technai 12 and Hitachi H9000-NAR operating at an accelerating voltage of 100 kV and 300 kV, respectively. Powder X-ray diffraction (XRD) was performed on a Bruker-AXS D8 general area detector diffraction system (GADDS), using Co K α radiation (1.790 26 Å) operating at 45 kV and 35 mA. The data were collected in the 2 θ range from 20° to 65° at an Ω angle of 15°.

Results

Figure 1 shows the shape evolution of titanium dioxide nanocrystals obtained adopting different relative amounts of LA

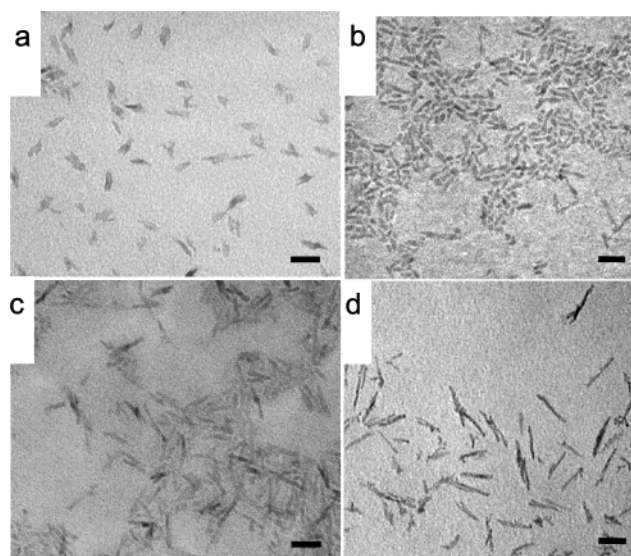


Figure 1. Shape evolution of TiO₂ nanocrystals by increasing LA concentration: (a) bullet- and diamond-shaped nanocrystals, (b) short rods, (c) long rods, (d) branched rods. Scale bar = 25 nm.

and TOPO, keeping the total surfactant amount constant. At low LA concentrations (2.0 mmol or lower), bullet- (3.5 × 12 nm) and diamond- (3.5 × 18 nm) shaped nanocrystals are obtained. By increasing the amount of LA to 4.0 mmol, the formation of rod-shaped nanocrystals with the diameter of 2.7 nm is observed. The rods length distribution is bimodal, with peaks at 14.3 and 21.8 nm. A further increase of the LA amount to 8.0 mmol (high LA concentration) leads to similar results: in this case, however, slightly longer rods with lengths of 16.9 and 28.2 nm are obtained. Finally, when a large excess of LA is used (~18.0 mmol), a mixture of nanorods and branched nanorods is observed.

The structural development of the various shaped nanocrystals was monitored via high-resolution TEM, and the images are reported in Figure 2 together with the corresponding simulated three-dimensional structures. The bullet- and diamond-shaped nanocrystals are elongated along [001] directions. A hexagon shape truncated with two {001} and four {101} faces (the [100] projection of a truncated octahedral bipyramid) is observed at one end of the bullet-shaped structures, the other end of the nanocrystal being faceted with two {101} faces. Likewise, a hexagon shape is observed at the center of the diamond-shaped structures, whose ends are both truncated with {101} faces.

The high-resolution analysis indicates that the rods obtained by increasing the LA concentration are also elongated along the <001> direction. The rods exhibit a zigzag pattern of {101} faces¹⁶ that can be regarded as repeating truncated octahedral bipyramid units. The unit is also observed at the center of the branched nanocrystals obtained at high LA concentrations. In this case, however, the arms grow out of the {101} faces of the seed.

X-ray diffraction spectra (Figure 3) of the samples indicate the presence of nanocrystalline anatase with a typical anisotropic growth pattern along the [001] direction. A gradual increase in the relative (004)/(200) intensities and a sharpening of the (004) peak is observed in the spectra as the nanocrystal shape evolves

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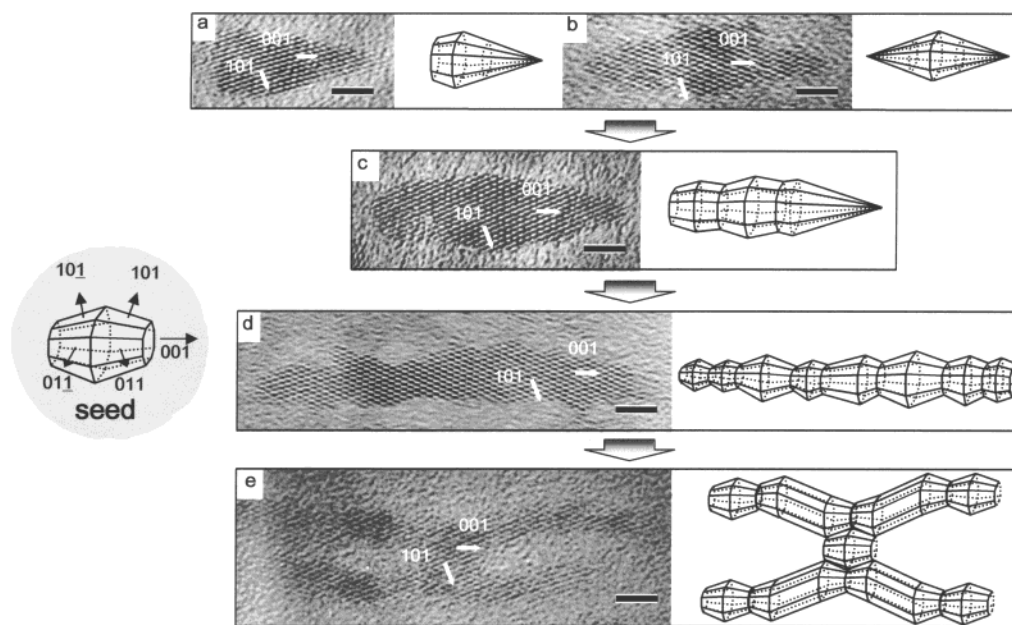


Figure 2. HRTEM analyses and simulated three-dimensional shape of (a) a bullet, (b) a diamond, (c) a short rod, (d) a long rod, and (e) a branched rod. The long axes of the nanocrystals are parallel to the c -axis of the anatase structure, while the nanocrystals are faceted with $\{101\}$ faces along the short axes. Hexagon shapes (the $[010]$ projection of a truncated octahedral bipyramid) truncated with two $\{001\}$ and four $\{101\}$ faces are observed either at the one end or at the center of the nanocrystals. The branched shape is a result of the growth along $[101]$ directions starting from the hexagon shape. Scale bar = 3 nm.

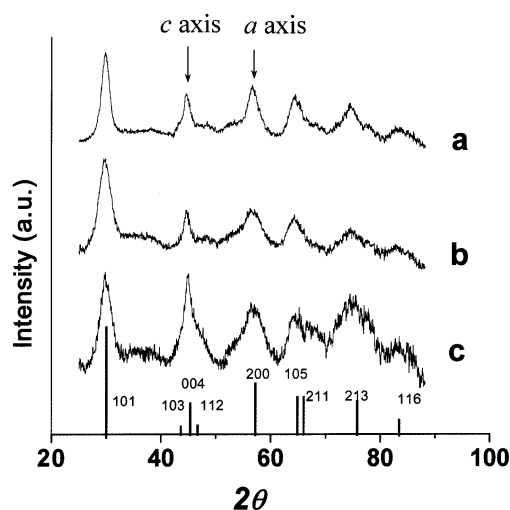


Figure 3. Powder XRD patterns of various shapes of titanium dioxide nanocrystals: (a) bullet and diamond shapes, (b) short rods, (c) long rods. The diffraction pattern of TiO_2 anatase is also reported as a reference.

from bullets and diamonds to short rods and long rods, as a consequence of the extended crystalline domain along the c -axis.

Figure 4 reports the statistical analyses of the crystal growth as a function of time for the rods obtained under high LA concentration (8.0 mmol). These data indicate that during the crystal growth stage the diameter of the rods is almost retained, while the length increases with growth time up to a saturation value. As mentioned previously, the rods have a bimodal size distribution, which is retained from very early to longer growth stages.

Discussion

The observed structural growth patterns suggest that the injection of the TTIO precursor into the reaction solution induces the formation of TiO_2 truncated octahedral bipyramid seeds terminated by $\{001\}$ faces with high surface energy and $\{101\}$

faces with relatively low surface energy.^{12,13} Then, the final shape of anatase nanocrystals is governed by the competition between the relative surface energies of the $\{001\}$ and $\{101\}$ faces and, therefore, the growth rate ratio between $[001]$ and $[101]$ directions (G_{001} and G_{101} , respectively).

In the absence of LA or at low LA concentrations (<2 mmol), the ratio between the growth rates along the $[001]$ and $[101]$ directions is larger than the ratio between the c and a lattice parameters ($G_{100} \gg 2.7G_{101}$), thus bullet and diamond shapes arise from the shrinking of the $\{001\}$ faces and the complete elimination of $\{001\}$ faces at one or two ends of the truncated octahedral bipyramid seed, respectively. The diamond shape allows the crystal to expose only $\{101\}$ faces, which are the lowest energy ones, as indicated by the fact that natural anatase crystals facet to expose 101 planes.¹⁴ At high LA concentration, however, LA selectively and strongly binds to the $\{001\}$ faces through a bridge-bonding mode^{14,17} and slows down the growth along the $\langle 001 \rangle$ directions. When the growth rate along the $[001]$ direction is close to 2.7 times that along the $[101]$ direction ($G_{100} \approx 2.7G_{101}$), two Ti layers grow along the $[001]$ direction during the time of four Ti layers' growth along the $[101]$ direction, according to crystal symmetry. Under this condition, monomers continuously grow further onto both $\{001\}$ faces and $\{101\}$ faces of the truncated octahedral bipyramid seeds, in such a way to expand the $\{101\}$ faces during crystal growth while preserving a constant $\{001\}$ surface area. However, when the $\{101\}$ surface area reaches a critical value under the kinetically driven regime, the formation of a step instead of further homogeneous expansion of $\{101\}$ surfaces leads to the growth of faceted rods.

In agreement with HRTEM observations, XRD peak broadening data indicate that by increasing the LA amount the crystal is progressively elongated along the $[001]$ direction. On the other hand, when a very large excess of LA is used (~ 18 mmol), the

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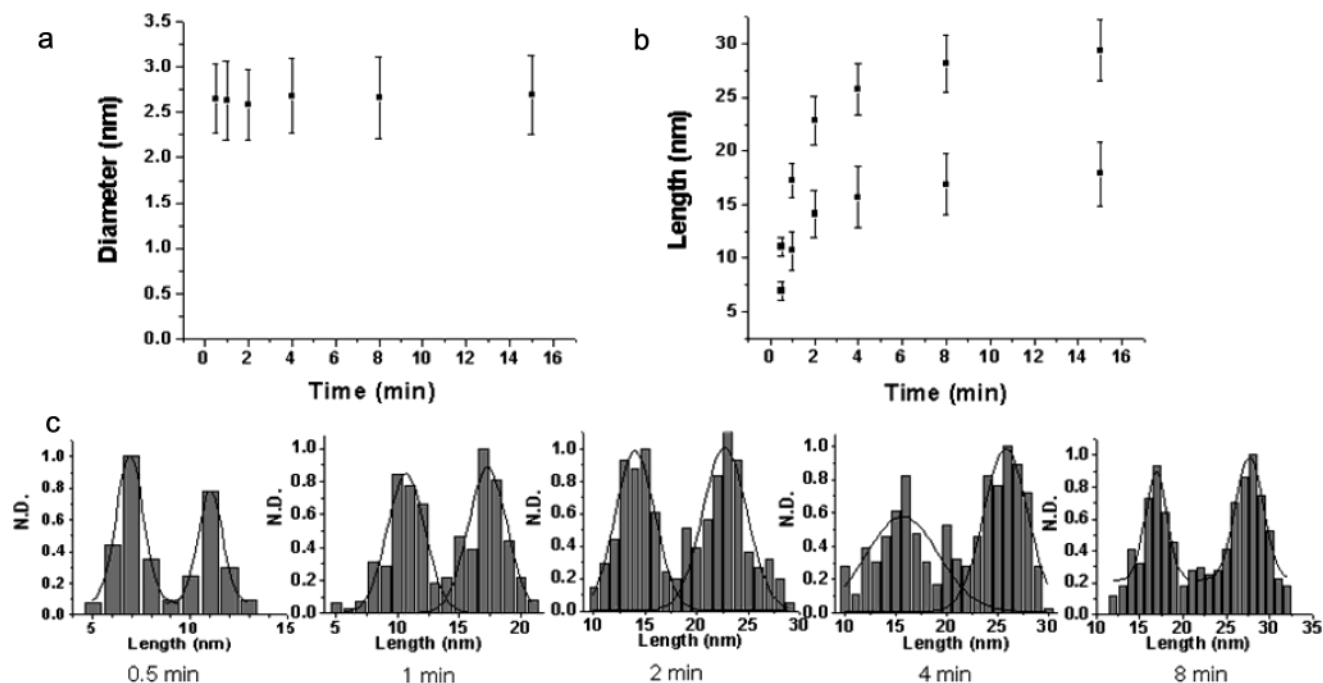


Figure 4. Statistical analyses of the size of long rods obtained at the LA concentration of 8.0 mmol as a function of growth time: (a) mean diameter distribution, (b) mean length distribution, and (c) length distribution.

growth along $\langle 001 \rangle$ directions is highly hindered and growth out of $\{101\}$ faces of seeds is favored, resulting in branched structures with various geometries.

By selectively binding to the $\{001\}$ faces, the effect of LA is also to slow the growth rates of these faces. As a consequence, under high LA amounts in order to have a growth of the $\{101\}$ surfaces without increasing simultaneously the $\{001\}$ surfaces, an anisotropic growth is favored with respect to an isotropic growth. The result is the observed rod structure elongated along the $\langle 001 \rangle$ direction with zigzag patterns of $\{101\}$ faces, allowing the increase of the $\{101\}$ surface area while preserving the (100) surface area.

It is noteworthy that the zigzag patterns observed are very similar to the ones obtained for titanium dioxide in hydrolytic media by oriented attachment.¹² In that case, the zigzag pattern arises from the alignment of truncated octahedral bipyramid units through an oriented attachment process, possibly mediated by surface oxygen (or hydroxyl) molecules. The attachment between truncated octahedral bipyramid units occurs at high energy facets, allowing the elimination of the surfaces at which the crystals join. The authors observed that the presence of surface-selective surfactants may hinder the oriented attachment during hydrothermal growth. Insights are offered on whether in the present case the mechanism responsible for the formation of the observed shapes is the anisotropic growth through addition of monomers onto the high energy surface or an oriented attachment mechanism can be obtained by the rod size distribution and growth pattern analysis. A bimodal length distribution is observed for the long rods, which could possibly be explained through both growth mechanisms. On the other hand, a bimodal length distribution is observed also in the short rods obtained by medium LA amounts, as well as in the sample obtained by low LA amounts where the two average sizes correspond to either bullet- or diamond-shaped nanocrystals (see Supporting Information). These data suggest that the bimodal size distribution arises from the growth out of either one or both (001) faces

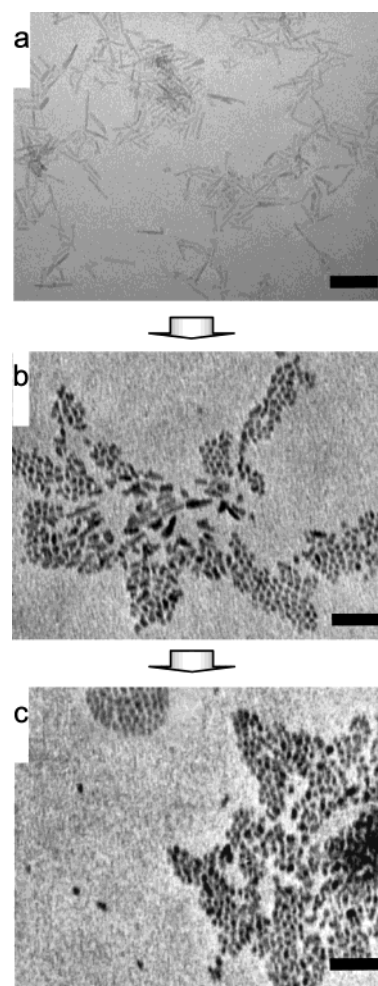


Figure 5. Time dependent shape evolution of TiO₂ nanorods: (a) 0.25 h, (b) 24 h, (c) 48 h. Scale bar = 50 nm.

of the seed. As the anatase structure is characterized by central

symmetry of along the [001] axes, the simultaneous growth on the two (001) faces would rather be expected.

A related effect is observed using excess LA conditions, where branched structures with less than four branches are observed (see Supporting Information), indicating an inhibition of growth on some of the (101) faces. Nonequivalent growth from equivalent faces has been already observed⁶ in the anisotropic growth of branched CdS nanocrystals. In that case, the temperature and concentration dependences show that this effect is attributable to a kinetically controlled growth.

The observed increase of the length of the rods as a function of time up to a saturation value provides further insight on the growth mechanism, suggesting the presence of a monomer growth process. When an oriented attachment mechanism is effective, an exponential (or linear) length dependence upon the growth time would be expected, as a result of the growth of nanocrystals occurring through attachment either between rods and rods or between rods and spheres.

The evolution of rods as a function of longer growth times was monitored by TEM analysis and is reported in Figure 5. The TiO₂ nanocrystals simultaneously convert from rods to small single crystalline spheres⁷ as a function of the growth time. This result indicates that the minimization of the overall surface energy is achieved preferentially by dissolution and regrowth of monomers during an Ostwald ripening rather than by interparticular aggregation processes^{12,18,19} such as oriented attachment.

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Conclusions

We report the shape evolution process of titanium dioxide nanocrystals in nonaqueous media in the presence of surfactants. The shape of the obtained nanocrystals evolves from sphere to bullet, diamond, rod, and branched rod, the growth patterns being determined by the minimization of the surface area associated with the high energy facet. The relative energy of the crystal facets can be varied exploiting crystallographically selective adhesion of surfactants, indicating that surface energy control by surfactant molecules is a powerful tool for tailoring nanocrystal shape even in the case of metal oxides.

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Supporting Information Available: Statistical analyses of the length distribution of the samples obtained at low and medium LA concentrations; TEM and HRTEM of branched structures with less than four branches. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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