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Cylindrical Polymer Nanostructures by Solution Template Wetting

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ABSTRACT: Wetting of porous templates, e.g., porous aluminum oxide with pore diameters in the range from 25 up to several 100 nm, by polymer melts has been demonstrated previously to be a highly effective way toward the preparation of polymer nanotubes. The concept evaluated in this contribution is to perform wetting from polymer solutions rather than from melts with particular emphasis on the influence of the molecular weight of the polymer used for wetting. Narrow molecular weight fractions were used for this purpose. The aim is to extend the nature of nanostructures which become available by wetting and to allow functionalization of the nanostructures by additives such as drugs or biological objects which decompose at elevated temperatures. Polystyrene was used as model polymer. Results are first of all that the quality of the solvent—good, Θ, or poor—and the polymer concentration are important wetting parameters as far as the preparation of stable cylindrical structures is concerned and second that nanowires, nanotubes, or cylindrical structures with a regular arrangement of voids can be prepared reproducibly by a proper variation of the molecular weight of the polymer used.

1. Introduction

The wetting of porous templates with polymer melts and solvents is a highly effective way to produce polymer nanotubes or nanorods.[1–12] Nanoporous aluminum or silicon templates with uniform pore diameters and high aspect ratios can be used as templates. The accessible pore diameters range from 25 to 100 nm. Individual nanotubes and nanorods or arrays of them are of interest for drug delivery applications, photonic crystals, sensor applications, catalysis, and optoelectronics as demonstrated in a set of papers.[1,2,13]

Depending on the used material nanorods or nanotubes can be obtained. Wetting with melts of low molecular weight organic materials, e.g., liquid crystals,[3] yields in nanorods and with high molecular weight polymers usually in nanotubes.[1,4,5] By varying the temperature[6] or using block copolymers,[7] nanorods consisting of high molecular weight polymers are obtained. Because of the high processing temperatures needed during the melt wetting process, it is difficult to produce functionalized nanotubes via melt wetting. McCarthy et al. introduced a functionalization after the wetting process.[8] Further structures, besides tubes and rods, could only be obtained by an additional annealing step after the nanotube production. Russell et al. obtained regular void structures by annealing polymer nanotubes.[9]

Another approach is the wetting of the template with solutions. Martin et al. filled the template pores with monomers and obtained nanotubes through polymerization of the monomers within the pores.[10,11] The wall thickness could be controlled via the polymerization time, up to a complete filling of the pores with polymer. Polymer nanotubes can be obtained by wetting with polymer solutions without additional treatment. By adding precursor materials like metal precursors or by wetting with polyacrylonitrile (PAN), inorganic nanotubes[2] and carbon nanotubes (CNTs), respectively, can be produced.[12] Russell et al. exploited this method for CNT production and observed the occurrence of instable structures when wetting with polystyrene (PS)−PAN block copolymer solutions below a certain concentration and after the removal of the PS and the corresponding transition into CNTs.

This paper concentrates on wetting from polymer solutions rather than from polymer melts since this method might be advantageous for a number of reasons. One reason is that the set of parameters which can be adjusted is higher than in melt wetting. Control parameters are the choice of the solvent, the polymer concentration controlling among other the viscosity and the quality of the solvent. Good solvents tend to cause a swelling of the polymer coils and bad solvents a chain contraction, and Θ solvents induce an ideal chain conformation as an intermediate state.[14,15] A key control parameter for wetting from solution is in particular the molecular weight of the polymer used. In fact, the molecular weight dependence of wetting is a major topic of this contribution using narrow molecular weight fractions for this purpose. A second reason for choosing the solution approach in wetting is that temperature-sensitive functional materials such as biological objects may be incorporated into the resulting nanostructures in this way, which fails in high-temperature melt wetting. Finally, a major reason for exploring the solution wetting approach is that we expect nanostructures like instable ones and void structures to become directly accessible in this way.

It is well-known that fluid films on solid surfaces are not necessarily stable and that dewetting processes may occur. These have been investigated in detail for planar surfaces.[16–18] Yet they also occur for fluid films inside cylindrical capillaries.[19,20] Dewetting is not the only process which may occur for fluid elements. Another is the onset of Rayleigh instabilities, i.e., the amplification of thickness fluctuations. Rayleigh instabilities have been considered primarily in the context of fluid threads yielding regular arrangements of fluid droplets.[21–23] Yet they also occur for thin films inside capillaries.[20] The decomposition of thin PMMA films attached to the surface of the pores of nanoporous templates via Rayleigh instabilities was studied, for instance, by Russell et al., who induced the decomposition by annealing the films at temperatures well above the glass transition temperature.[9] He observed in this case the formation of nanotubes with a regular void structure.

It seems feasible, among others because of the reduced viscosities of the solutions and variations in wetting properties induced by the solvents, that such processes may also play a significant role in structure formation via solution wetting of nanoporous templates. Complex cylindrical nanostructures resulting from a superposition of wetting, dewetting, and Rayleigh instabilities can be expected to form and to be isolated due to the evaporation of the solvent and the corresponding solidification of the remaining polymer material. Major param-

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Table 1. Types of Cylindrical Nanostructures Available from Solution Wetting for Various Molecular Weights of PS

mol wt (g/mol)	rods	regular void structures	tubes
1 890	×		
4 850	×		
7 000	×		
17 300		×	
35 600		×	
75 000		×	
96 000		×	
133 000			×
184 000			×
248 000			×
319 000			×
601 800			×

eters to vary are the polymer concentration, the quality of the solvent, and the molecular weight of the polymers used.

For the investigations to be reported in the following we decided to use polystyrene (PS) as model polymer system for a number of reasons. Narrow molecular weight distributions of PS are available for a broad range of molecular weights covering the range from a few 1000 g/mol up to a several 100 000 g/mol. PS solutions can be prepared displaying good, bad, or Θ solvent conditions by specific choices of the solvents or solvent mixtures and temperatures which directly affects the specific chain conformations—swollen, collapsed, or ideal conformation.[14,15] Another important parameter in these investigations is the polymer concentration. Dilute polymer solutions are characterized by individual, nonentangled chains whereas polymer chain entanglement sets in as a critical concentration is surpassed. Both the chain conformations and the presence or absence of entanglements should affect wetting, subsequent instability processes, and thus the architecture of the resulting cylindrical nanoobjects.

2. Experimental Section

PS with polydispersities below 1.1 were purchased from Polymer Standard Service. The PS fractions used for the experiments were characterized by weight-average molecular weights ranging from about 2000 up to about 600 000 g/mol. Details on the specific molecular weight fractions used are given in Table 1.

HPLC grade cyclohexane from Fluka was used as solvent for the preparation of the wetting solutions. The solutions were kept at temperatures of 301 K (poor solvent situation), 308 K (Θ-solvent situation), or 313 K (good solvent situation) during the wetting process. The polymer concentrations chosen were 3, 7, and 10 wt %. For the investigations varying the molecular weight dichloromethane was used as solvent with a polymer concentration of 5 wt %.

The aluminum templates were obtained from the Max Planck Institute of Microstructure Physics in Halle. The average pore diameter amounted to 400 nm and the pore depth to 1 μm. However, the diameters of the pores were subjected to considerable variations extending from about 150 to 560 nm. This allowed us to investigate the influence of the pore size on structure formation within one and the same wetting experiment. Furthermore, the templates contained branches and other defects.

For solution wetting the templates were either immersed for 1 h within the wetting solution and subsequently removed from the solution, or the solution was dropped in several steps on the template. The wetted templates were dried at room temperature or at elevated temperatures, the polymer layer on top of the template was mechanically removed, and the template was then removed by dissolving it in an aqueous 10 wt % potassium hydroxide solution.

The resulting PS nanostructures were analyzed by scanning electron microscopy (Hitachi S-4100) and transmission electron microscopy (Jeol JEM 3010). To enhance the contrast, the PS was stained by adding palladium acetate to the PS solution prior to wetting. The palladium acetate was subsequently reduced to yield palladium nanoparticles dispersed within the PS nanostructures.

3. Results and Discussion

3.1. Influence of the Solution Concentration in the Structure Formation. The influence of solution concentration in wetting and the corresponding structure formation was evaluated for a limited number of molecular weights of PS (75 000, 432 000, and 819 000 g/mol). Independent of the molecular weight, unstable cylindrical nanostructures were obtained for polymer concentrations below 10 wt %. Completely collapsed structures were accessible from solutions with 3 wt % PS (Figure 1a). Using 7 wt % solutions, partially collapsed structures formed (Figure 1b) and stable structures were provided from 10 wt % polymer solutions (Figure 1c). The interpretation is that for lower concentrations probably individual or only slightly entangled chains are adsorbed on the surface of the pores yielding structures with poor mechanical properties.

3.2. Influence of the Solution Quality of the Solvent in the Structure Formation. For a given polymer concentration the result is that wetting performed from polymer solutions in which the polymer coils are collapsed (poor solvent condition) yields unstable structures, which collapse when extracting them from the pores. An example is shown in Figure 2a for wetting with a 10 wt % solution of PS under poor solvent conditions (301 K, cyclohexane). Somewhat more stable objects result for Θ conditions (308 K, cyclohexane) (Figure 2b). In this case tubes may form, with mechanically stable tops and bottoms, which are a perfect copy of the hemispherical shape of the pore bottoms. The remaining parts of the tubes collapse on extraction. This even holds true for polymer concentrations amounting to 10 wt % which are used in the following to prepare stable structures from good solvents (313 K, cyclohexane) (Figure 2c). Again, the molecular weight of the PS selected for the wetting studies does not play a major role with respect to the nanostructure stability.

Finally, stable cylindrical polymer nanostructures are formed if wetting takes place in good solvent conditions provided that the polymer concentration is well above the limit discussed in the previous section (Figure 2c). So in the following only the case of good solvent conditions will be treated for a given and fixed concentration. The solvent was changed to dichloromethane for practical reasons which allowed a polymer concentration well above the critical one of only 5 wt %. The parameter to be modified is the molecular weight.

3.3. Influence of the Molecular Weight in the Structure Formation. The experimental result to be discussed in the following in more detail is that structure formation by solution wetting is primarily controlled by the molecular weight when keeping the quality of the solvent and the solution concentration constant. Three main types of nanostructures formed by wetting are observed, namely solid nanorods, nanotubes, and cylindrical nanostructures with a periodic arrangement of voids along the axis. The correlation between the molecular weight used for wetting and the structures formed via wetting is displayed in Table 1. Solid nanorods are predominantely observed for molecular weights in the range up to 7000 g/mol, regular void structures from about 17 000 g/mol up to about 75 000 g/mol, and finally nanotubes above this range of molecular weights. It has to be pointed out, however, that these three types of structures are not strictly confined to the molecular weights specified above. Each of them may also be observed outside the ranges, yet the probability for the formation of such structures outside the specified ranges is low. These three types of structures will be discussed in some detail in the following.

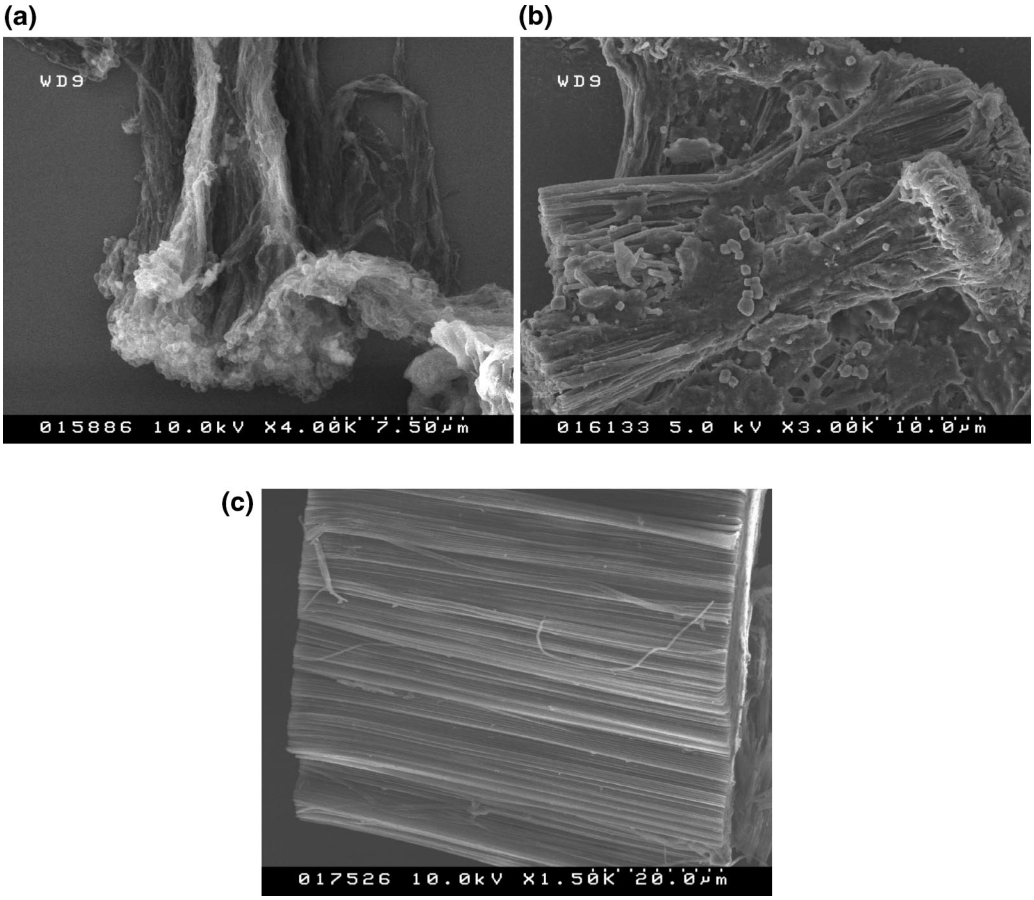

Figure 1. Nanostructures resulting from solution wetting for (a) 3, (b) 7, and (c) 10 wt % solutions of polystyrene for good solvent conditions (313 K, cyclohexane). The nanostructures shown in (a) and (b) are collapsed.

3.4. Nanotube Formation: Wetting by Polystyrene with Molecular Weights above 75 000 g/mol. Wetting of porous templates with solutions containing PS with molecular weights above about 75 000 g/mol is found to give rise to the formation of a thin wetting layer within the pores similar to the case of wetting by polymer melts. Polymer nanotubes can thus be extracted from the template. Figure 3 displays examples for such tubes for PS of two different molecular weights.

Wetting takes place for all pore diameters available from the templates in this range of polystyrene molecular weights. Pores with diameters ranging from 150 to 560 nm give rise to polymer nanotubes with corresponding outer diameters (Figure 4a). Nanotubes with homogeneous wall thickness are formed in all cases independently of the molecular weight of the polystyrene used in the wetting solutions. It is, however, obvious that the wall thickness varies with the pore radius. This is analyzed below in more detail. An interesting observation is that a homogeneous wetting also takes place at branches within the pore structure. Such branches show up as branched nanotubes as shown in Figure 4b. The thickness of the walls quite obviously varies along the branches in the same way as the radius of the several branches.

It has already been pointed out that the thickness of the solidified wetting layer within the pores and thus of the resulting nanotubes does not seem to stay constant as the pore radius varies, and it seems furthermore possible that the same holds for a variation of the molecular weight of the polystyrene. The analysis of the wall thickness as a function of these two parameters at a constant concentration of the wetting solution gives rise to the correlations result as displayed in Figure 5.

Figure 5 shows first of all that the molecular weights of the polystyrene used for wetting does not play a significant role as far as the thickness of the walls is concerned. All molecular weight fractions of polystyrene give rise to the same wall thickness for a given pore radius. The thickness of the layers thus has no correlation to the diameter of the chain molecules—adsorption of a single chain arrangement—or to the length of the chains. Second, this analysis reveals that the pore/tube radius is the principal parameter which controls the wall thickness. The thickness amounts in all cases to a value of about 50−60% of the pore radius. This even holds for the branched structure shown in Figure 4. One assumption to be discussed below in more detail is that dewetting takes place and controls the layer thickness to a certain extent.

3.5. Nanorod Formation: Wetting by Polystyrene with Molecular Weights below 7000 g/mol. Wetting of the templates from solutions containing molecular weight fractions of PS below 7000 g/mol tends to give rise to a complete filling of the pores and thus, after extraction of the solid PS, to the formation of polymer nanorods. Solution wetting resembles in this respect melt wetting, where the formation of nanorods is observed for oligomeric systems. Figure 6 shows nanorods obtained in this way. The observation is furthermore that nanorod formation happens independently of the pore diameter for all molecular weights, the rod diameter being directly controlled by the pore radius.

In many instances these rods do not seem to be completely solid but rather contain small holes distributed irregularly within the rods. Furthermore, their sizes do not seem to bear any correlation with the rod diameter. The tentative interpretation is that they are probably defects resulting from an incomplete filling or originate from defects of the template structures. Wetting from solution thus agrees qualitatively with wetting

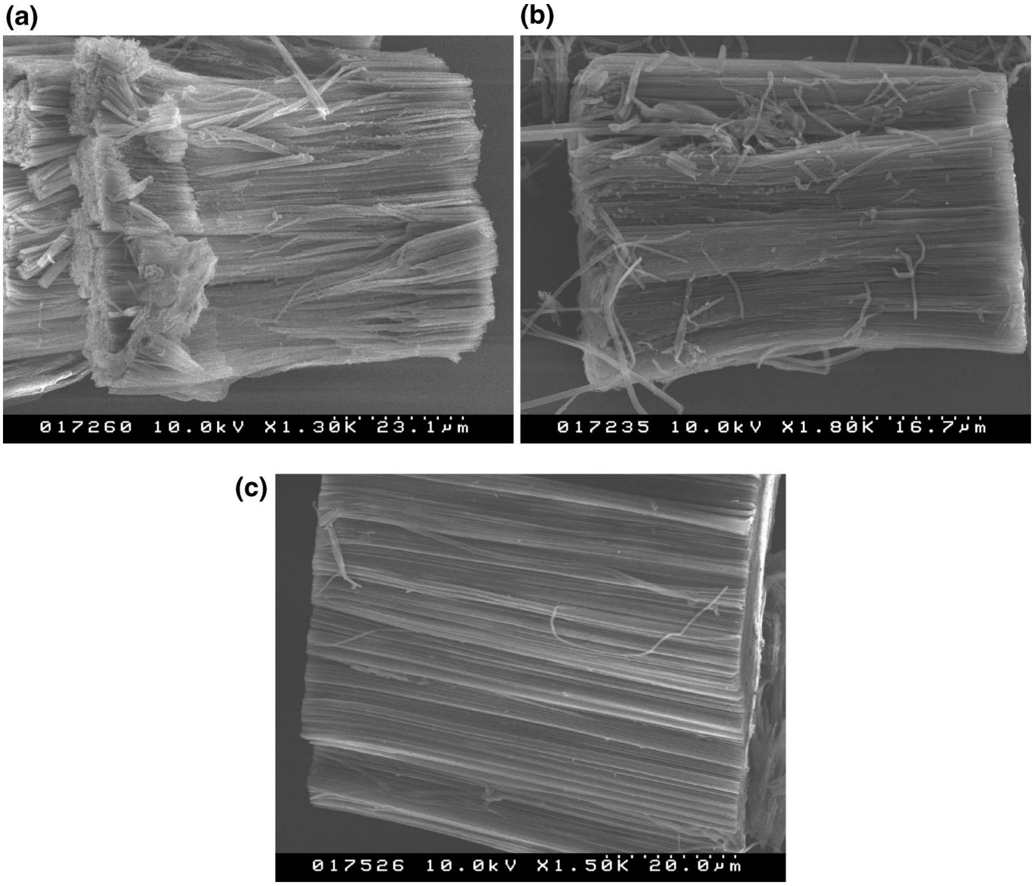

Figure 2. Nanostructures resulting from solution wetting: 10 wt % polystyrene for (a) poor, (b) Θ, and (c) good solvent conditions (301, 308, 313 K; cyclohexane). The nanostructures are collapsed for (a) and (b).

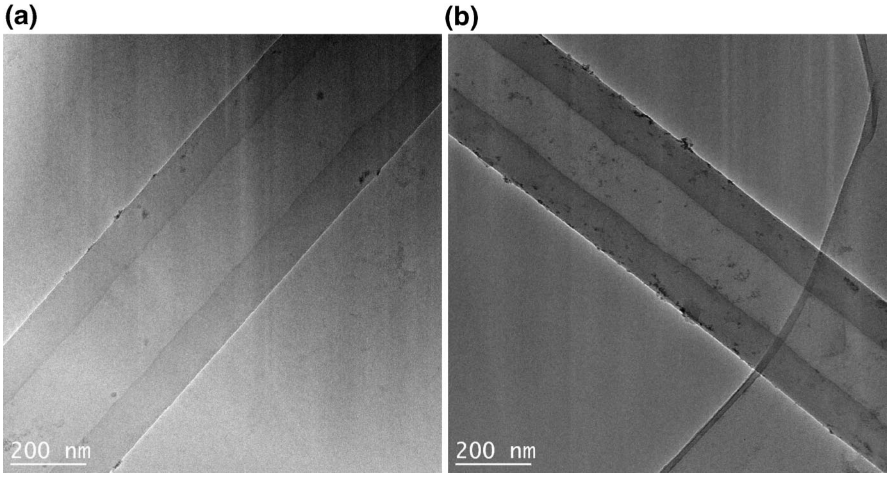

Figure 3. TEM images of nanotubes obtained via wetting from solution containing high molecular weight fractions of polystyrene: (a) 96 000 g/mol; (b) 133 000 g/mol.

from the melt where complete filling of the pores and nanorod formation has been observed for low molecular weight systems including oligomer systems.

3.6. Formation of Nanorods with a Regular Void Structure: Wetting by Polystyrene with Molecular Weights in the Intermediate Range from 7000 to 75 000 g/mol. The use of intermediate molecular weight PS results in polymer structures which differ strongly from the ones which are directly available from melt wetting. This is obvious from Figure 7, which displays some of the structures resulting from solution wetting and a subsequent extraction.

It is obvious that regular void nanostructures are formed in which voids are regularly spaced along the length of the nanorod. In general, the voids are located within the cylindrical objects and fully enclosed by the polymer so that the outer wall is completely given by polystyrene. Yet one also finds objects in which the voids extend to the surface of the cylindrical objects as shown in Figure 8.

The diameter of the voids and the distance between them seem to be related to a certain extent to the radius of the nanostructure and thus of the pore from which it came from prior to the extraction. These data are collected in Figure 9.

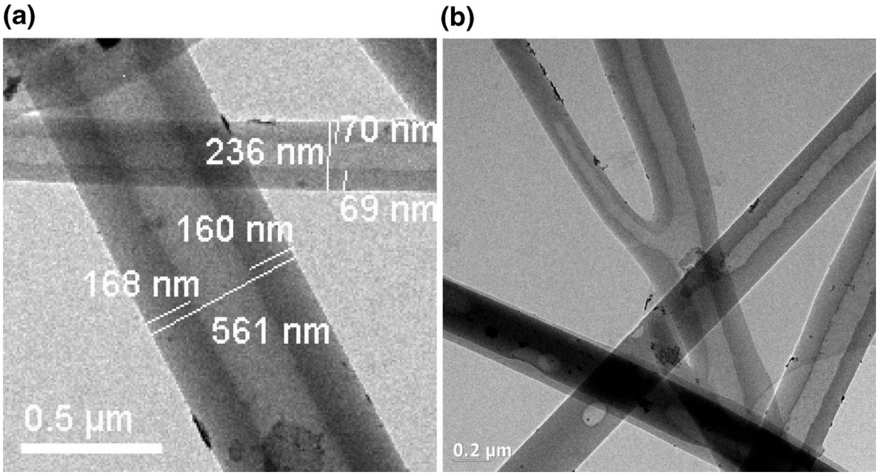

Figure 4. (a) Nanotubes with different diameters and wall thicknesses. (b) Branched nanotubes originating from branched pores within the template; the wall thickness changes as a function of the radius of the tubular structures.

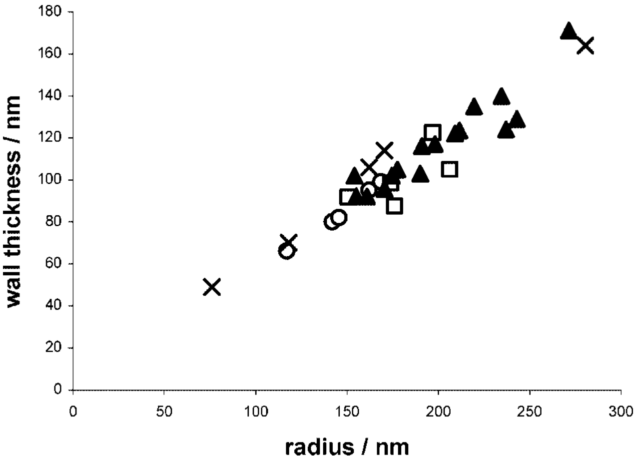

Figure 5. Dependence of the wall thickness of the nanotubes on the pore radius obtained for different molecular weight fractions of PS. Crosses (×) represent nanotubes made from PS with a molecular weight of 133 000 g/mol, circles (●) represent tubes consisting of PS with a molecular weight of 248 000 g/mol, squares (■) represent tubes made of PS with a molecular weight of 319 000 g/mol, and triangles (▲) represent tubes made from PS with molecular weights from 1.890 to 601 000 g/mol.

It is obvious that a certain correlation exists: the spacing of the pores increases with increasing radius of the cylindrical structures obtained by solution wetting. The ratio of the distance between the voids and the radius r is ~3.8.

3.7. More Detailed Discussion of the Experimental Results. Three types of structure formation have been observed for solution wetting: nanorods, nanotubes, and void structures. In the following we will discuss these three types of structures considering models which possibly explain their formation.

Nanorod Formation. As already pointed out, wetting from solution agrees qualitatively with wetting from the melt where a complete filling of the pores and the formation of nanorods have been observed for low molecular weight systems including oligomer systems. The assumption is that wetting takes place layer by layer until the pores are completely filled with the polymer species.

Nanotube Formation. It was observed that the wall thickness is only dependent on the tube radius and independent of the molecular weight. A dewetting process may be the reason why the thickness of the wall formed in nanotube formation does not depend on the molecular weight but rather on the tube radius. The driving force for dewetting is predicted to increase in capillaries with increasing film thickness, in contrast to the case of planar surfaces where the corresponding driving force decreases with increasing film thickness. The theoretical treatment is limited to relative film thicknesses smaller than the one considered here. Yet a possible qualitative interpretation is that curvature plays a role in a way that a given ratio of film thickness to tube radius is kinetically the most stable and controls the thickness observed in the structures originating from wetting. Wetting is enhanced as the layer thickness increases in capillaries contrary to the case of planar substrates.[19,20] It seems possible that wetting is also enhanced with increasing curvature of the capillaries for a given thickness of the films. The combination of these two processes may be one factor which controls—probably kinetically—the constant ratio between film thickness in the capillaries and the radius of the capillary. In fact, sequences of cylindrical structures have been observed which are in agreement with the ones predicted by theoretical treatments of dewetting in capillary systems (Figure 10).

Void Structures. A straightforward interpretation for the nanostructures with regular arrangement of voids resulting for wetting from solutions containing PS fractions of intermediate molecular weight is that they originate from Rayleigh instabilities to which cylindrical structures with wall coverage are subjected. First of all, this interpretation can account for the observation of periodic thickness undulations of the PS wall in the corresponding nanotube, which corresponds to an early stage of development of the instability. An example is shown in Figure 11.

The also observed periodic arrangement of voids along the axis of the cylindrical nanostructures would correspond along this line to a later stage of development. In principle, a theory is available to predict what kind of structures should result from Rayleigh instabilities. The experimental data on void formation by Rayleigh instabilities do not correspond in absolute numbers to those predicted by theory, which is not really surprising in view of the fact that the theory concentrated on film thicknesses that are small compared to the pore diameters. This is not valid in our case, and in fact, it also did not hold for the annealing studies performed by Russell et al.[9] They observed a ratio of the void distance to the nanostructure diameter of about 5.5, whereas here we find a value of the order of 4. Clearly, the extension of the theories to thicker walls is needed. Nevertheless, it is interesting to point out that assuming an original wall thickness of the tubular structure prior to the onset of Rayleigh instabilities as observed for the nanotubes one can predict a relative void distance d/r

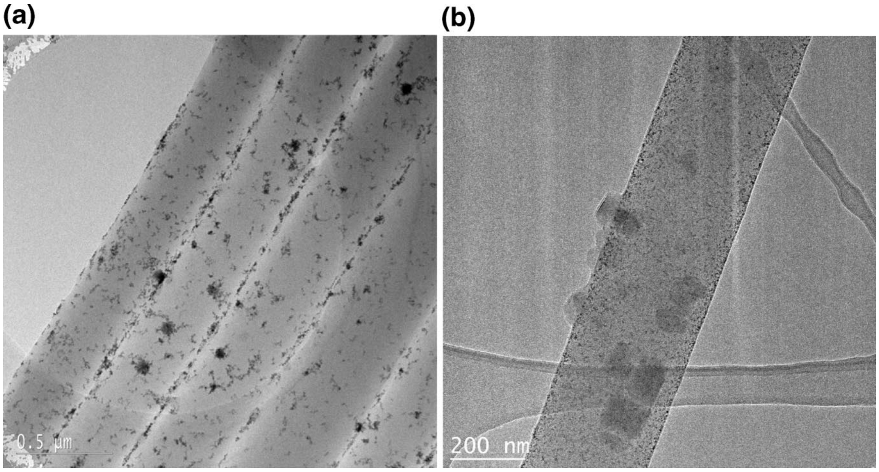

Figure 6. Nanorod formation taking place in solution wetting for low molecular weight fractions of polystyrene: (a) molecular weight 4850 g/mol; (b) molecular weight 1890 g/mol.

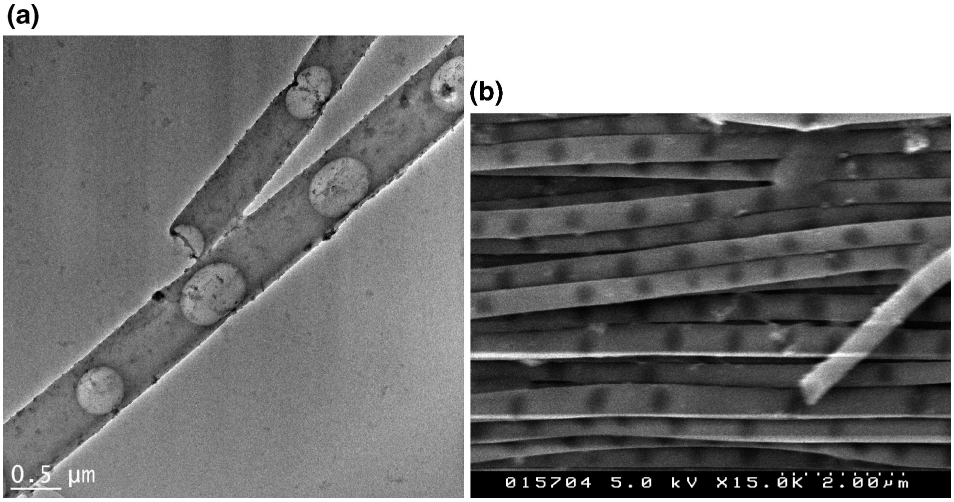

Figure 7. Polymer nanostructures resulting from solution wetting for molecular weight fractions with intermediate molecular weights of 35 600 g/mol: (a) TEM image, (b) SEM image.

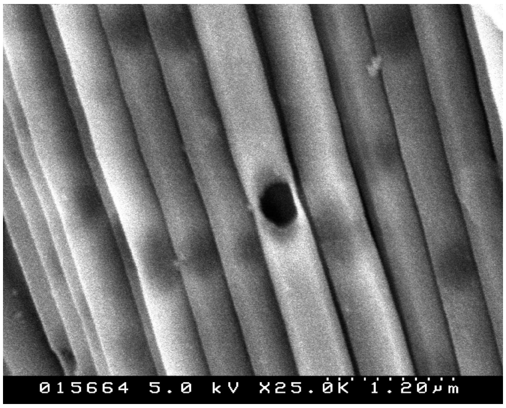

Figure 8. SEM image of void structures where the voids extend to the surface of the cylindrical objects (polystyrene with a molecular weight of 75 000 g/mol).

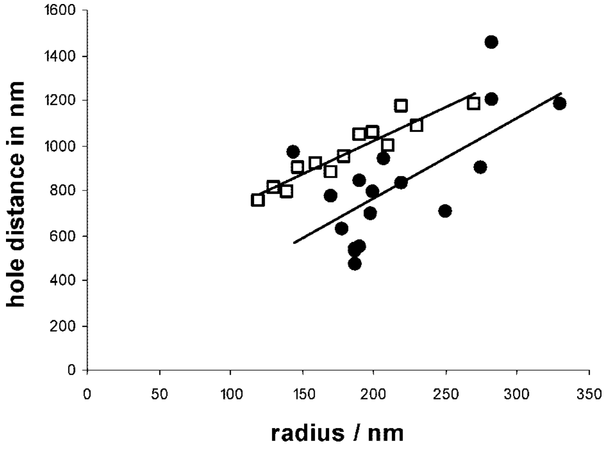

Figure 9. Correlation between void spacing and pore radius (●). Data are also included from ref 9 (□).

of about 4 by just assuming volume conservation during the transition from the tubular to the void structure. Furthermore, the cylindrical structures with circular holes within the walls allowing access from outside as well as the formation of elongated compartmented structures might correspond to a coarsened stage of this process where dewetting has set in to a certain degree.

4. Conclusions

In this work solvent wetting of porous templates was investigated. Different parameters like the polymer concentration, the solvent quality, and the molecular weight were varied independently from each other, and the resulting structures were examined. From polystyrene solutions with

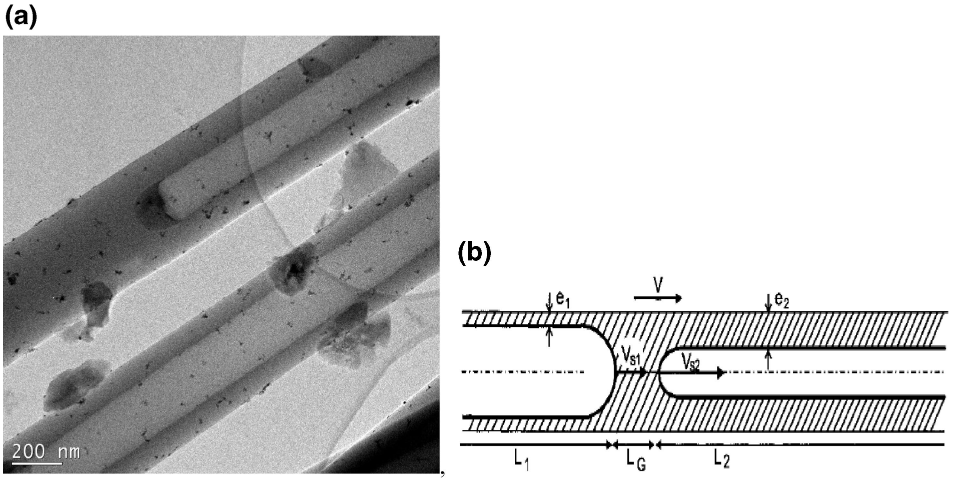

Figure 10. Sequences of cylindrical structures (a) are observed which agree with the ones predicted by theoretical treatments of dewetting in capillary systems (b).[19]

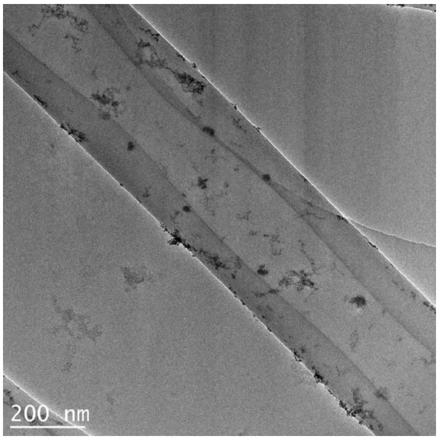

Figure 11. Thickness undulations of polystyrene walls.

low polymer concentrations instable cylindrical structures were obtained. These were also achievable from polymer solutions with poor or Θ-solvent conditions. Through solvent wetting from good solvent conditions and sufficiently high polymer concentrations stable cylindrical structures were obtained. Depending on the molecular weight different structures were formed. From polystyrene solutions with low molecular weight polystyrene solid nanorods were formed. Using polystyrene with a high molecular weight nanotubes were accessible, and from intermediate molecular weight polystyrene regular void structures were obtained. The range of accessible cylindrical nanostructures could be expanded through solvent wetting.

The results reported in this paper clearly show that wetting of porous templates from polymer solutions offers a further potentially useful approach toward specific nanostructures in addition to the one based on polymer blends. The wide range of possible applications of such nanoobjects has been already discussed in the publications referring to melt wetting introduced above. An interesting effect which needs further evaluations is that the three modes of structure formation, i.e., rods, void structures, and nanotubes, while occurring predominantly for specific molecular weight fractions also show up occasionally outside these specific ranges. The individual structure formation processes thus seem occasionally to be unstable versus branching into other structure formation modes.

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