Formation of Two-Dimensional Array of Multiwalled Carbon Nanotubes in Polystyrene/Poly(methyl methacrylate) Thin Film

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Introduction. Carbon nanotubes (CNTs) have been investigated for such diverse applications as nanoscale electronic devices,[1,2] field effect transistors,[3] chemical sensors,[4] and polymer nanocomposites[5,6] due to unique electrical and mechanical properties as well as an unusually high aspect ratio. However, because of strong intertube van der Waals interactions, the dispersibility of CNTs in ordinary solvents is so poor that it is extremely difficult to disperse and manipulate CNTs well.[7,8] Many research groups have attempted to disperse CNTs uniformly either in aqueous solution or in various organic liquids, by modifying the surface of CNTs via the covalent method (chemical surface modification)[9−12] or noncovalent method.[7,8,13−18] Although many studies have focused on the exfoliation and dispersion of CNTs, only a handful of results were able to demonstrate structural arrays of dispersed CNTs on organic or inorganic substrates. For example, Snow and co-workers[19] studied formation of carbon nanotube networks (CNNs) that were prepared by liquid deposition of CNTs dispersed in water onto either the silicon wafer or polymeric substrates. Here, CNTs were suspended in surfactant-containing water by ultrasonication until the pretreated substrate was immersed to deposit CNTs on its surface. Even though CNNs, which are prepared by liquid deposition method, can be utilized as organic transistors, it is difficult to control the structure and/or the density of CNNs and to produce large quantities of CNNs. In this communication, we demonstrate a neat approach to forming two-dimensional arrays of multiwalled carbon nanotubes (MWNTs) on the silicon wafer from an immiscible polymer pair of polystyrene (PS) and poly(methyl methacrylate) (PMMA). We found that MWNT assembled at the surface of silicon wafer from a MWNT-PS nanocomposite/PMMA mixture where some of PS chains are grafted to MWNT and a random network of MWNT was assembled.

Experimental Section. MWNTs (purity >95%, Iljin Nanotech, Korea) were treated by a reflux of 3 M HNO_3, followed by a reflux of 5 M HCl, to eliminate any residual impurities without causing damage to MWNTs.[20] The acid-treated MWNTs were dispersed in styrene monomer, which was then in-situ polymerized at 65 °C for 24 h in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator. The molar ratio of styrene over AIBN was 80. During the polymerization, the reactor was immersed in an ultrasonic generator which was operated at a normal frequency of 28 kHz with a power of 600 W. The product of the polymerization was a nanocomposite of MWNT and polystyrene. The same procedure was employed to synthesize MWNT−poly(methyl methacrylate) (PMMA) nanocomposites and reported elsewhere.[5] A 50:50 (by weight) mixture of the MWNT−PS nanocomposite and poly(methyl methacrylate) (PMMA) (M_w = 76 700, M_w/M_n = 1.06) was prepared in toluene, and an ultrathin film was obtained by spin-casting of the mixture solution on the hydrophilic silicon wafer at 2500 rpm for 2 min at room temperature. Prior to spin-casting, silicon wafers were cleaned in a mixed solution of H_2SO_4 and H_2O_2 (70:30 by vol) and then rinsed in deionized water several times. The film was estimated to be ca. 30 nm thick by ellipsometry. Morphological investigation of the surface of the 50/50 MWNT−PS nanocomposite/PMMA blend film was made by the dynamic mode atomic force microscopy (SPA400 with SPI 4000 controller, Seiko Instruments). The cantilever was fabricated from Si_3N_4, and the tip was SI-DF40 (spring constant: 42 N/m; resonance frequency: 250−360 kHz). To determine the composition profile of the blend film surface, the film was etched by selective solvents. For example, PS and PMMA phases were etched by cyclohexane and acetic acid, respectively. The final MWNT array on the silicon wafer was investigated by a scanning electron microscope (SEM, Hitachi S-4200) at 15 kV of acceleration voltage. The sample was gold coated to minimize the charging effect.

Table 1. Molecular Weights of PS in the MWNT−PS Nanocomposite

	MWNT content (wt %)			
	0	0.05	0.1	0.2
M_w	45900	46300	64800	90600
M_w/M_n	1.99	2.18	3.14	5.03

Results and Discussion. In the MWNT−PS nanocomposite, it is believed that there are not only polystyrene molecules free from the MWNT but also polystyrenes that were grafted onto the MWNT. During the in-situ polymerization of monomers in the presence of AIBN as an initiator and MWNTs, AIBN radicals not only initiate the polymerization of monomers in the bulk but also were reported to trigger the growth of polymer chains on the surface and/or at the ends of MWNT.[5,21] Therefore, if the concentration of MWNT in the monomers increases, the amount of AIBN available to MWNT would also increase, leading to a decrease in the AIBN concentration available for the polymerization of styrene monomers in the bulk. Table 1 shows the molecular weight and the polydispersity of PS in the MWNT−PS nanocomposite. The MWNT−PS nanocomposite was dissolved in THF, and the solution was carefully filtrated so that polystyrenes that are free from MWNT are collected. The molecular weight of those polystyrenes was measured by GPC. Both the molecular weight and the polydispersity of PS increased with an increase in the MWNT concentration, which indirectly showed that some of initiators were consumed by MWNTs and there were some PS chains grafted onto MWNT (MWNT-*g*-PS) in the MWNT−PS nanocomposite.

Additional evidence of the presence of the MWNT-*g*-PS is presented in Figure 1. The acid-treated MWNTs that were blended with PS were not dispersed well in toluene; they were in fact precipitated in short time, as

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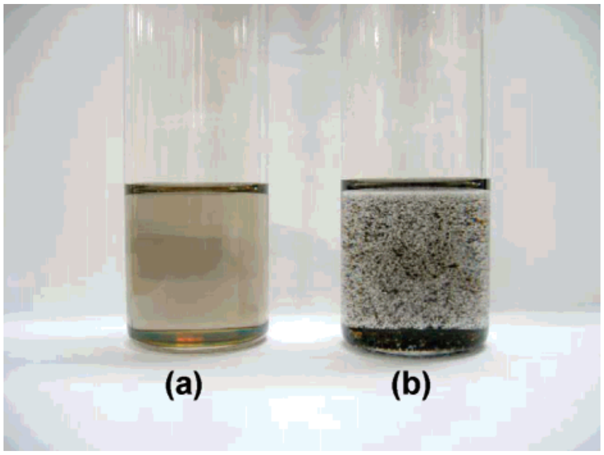

Figure 1. Toluene dispersion (solution concentration = 9 mg/mL) of (a) MWNT(0.1 wt %)−PS nanocomposite and (b) acid-treated MWNT (0.1 wt %) blended with PS.

shown in Figure 1b. However, the toluene solution of the MWNT−PS nanocomposite in Figure 1a yielded a homogeneous dispersion, which indicates that some polystyrene chains are grafted onto the MWNT.

Figure 2a shows the AFM image of the spin-cast film of MWNT(0.1 wt %)−PS nanocomposite/PMMA (50/50, w/w) blend, which is very smooth and homogeneous except for a few nanometer-scale islands. It is quite unusual for a spin-cast film of an immiscible polymer blend to show such a homogeneous surface morphology. In general, a thin film of the spin-cast immiscible polymer blend is far from a thermodynamic equilibrium state due to the rapid evaporation of the solvent during the spin-casting process; thus, complete phase separation or dewetting cannot occur.[22,23] Indeed, it has been shown that a sea island, or continuous island, or pitted morphology was observed for the PS/PMMA blend film resulting from the partial phase-separation phenomenon, although the blend composition and the type of the solvent and the substrate can affect the morphology.[24−26] To determine the composition profile of the spin-cast film as a function of the film depth, we sequentially etched the blend film with selective solvents. First, the film was etched by acetic acid, which is a good solvent for PMMA and a nonsolvent for polystyrene. The surface topography of the film did not change much upon etching, except that some nanometer-scale holes were formed, as the small amount of PMMA on the film surface was dissolved away (Figure 2b). Total film thickness remained almost constant after the etching with acetic acid. When the same spin-cast film was etched by cyclohexane, however, the thickness of the film decreased by about 10 nm, as shown in Figure 2c. The surface of the etched film was once again smooth without any evidence of phase separation. Because only polystyrene can be dissolved in cyclohexane, the air surface of the spin-cast MWNT−PS nanocomposite/PMMA blend film was believed to the polystyrene, and the thickness of the polystyrene layer was about 10 nm. Figure 2d is the AFM image of the film that was etched by acetic acid, dried, and then etched again by cyclohexane. The image in Figure 2d is almost identical to that in Figure 2c, confirming that the air surface of the cast film was indeed polystyrene. To investigate further the structure within the film, the polystyrene-removed film (Figure 2c) was dissolved in acetic acid, which would etch away PMMA. A two-dimensional array of nanowires, so-called CNNs, on the

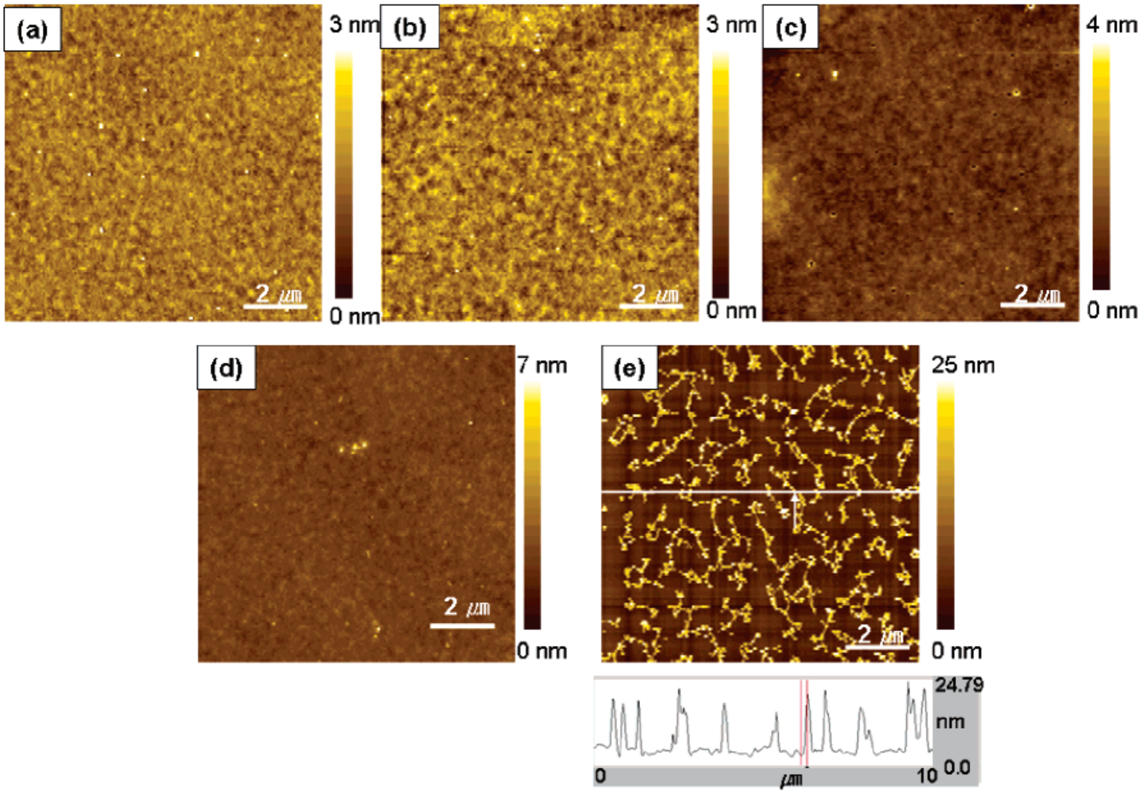

Figure 2. AFM images of MWNT(0.1 wt %)−PS nanocomposite/PMMA (50/50, w/w) blend films: (a) as-cast film (rms rougness = 0.38 nm), (b) upon etching the film in (a) by acetic acid (rms roughness = 0.40 nm), (c) upon etching the film in (a) by cyclohexane (rms roughness = 0.34 nm), (d) upon etching the film in (b) by cyclohexane, and (e) upon etching the film in (c) by acetic acid (rms roughness = 6.0 nm).

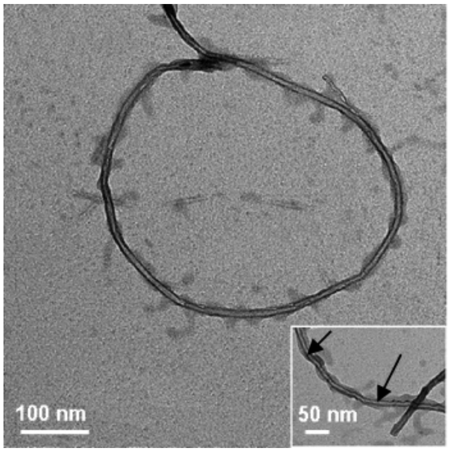

Figure 3. TEM photograph of MWNT(0.1 wt %)−PS nanocomposite/PMMA (50/50, w/w) blend film that was etched by cyclohexane and then by acetic acid.

silicon wafer was obtained, as shown in Figure 2e. The diameter of these nanowires was 10−15 nm, which was nearly identical to that of the pristine MWNT.

The nanowires were very stable, firmly attached to the silicon wafer, and could not be removed easily. Thus, it is believed that the nanowire array on the silicon substrate was the result of the uniform dispersion of MWNTs in the MWNT−PS nanocomposites. It should be noted that there are end-grafted polystyrene molecules on the MWNT, as stated earlier. Also, the MWNT−PS nanocomposite/PMMA blend film was shown to be composed of a phase-separated bilayer structure: a thin, MWNT-containing PMMA layer next to the silicon substrate and a polystyrene layer on top of the PMMA layer, both of which are lying parallel to the substrate. Impurities embedded in the polymers have been reported to accelerate dewetting of the thin polymer films.[27,28] We believe MWNTs in our MWNT−PS nanocomposite helped the phase separation of polystyrene and PMMA. More direct evidence of the formation of the MWNT−PS nanowire arrays was obtained by TEM.

Here, the toluene solution of the MWNT−PS nanocomposite/PMMA blend was spin-cast directly on the TEM grid and was sequentially etched by cyclohexane and acetic acid in exactly the same manner as described earlier. Figure 3 unequivocally shows a flexible, single strand of MWNT and the polystyrene chains wrapping around the MWNT (arrows in the inset). Therefore, we could conclude that the nanowire array observed on the silicon by AFM (Figure 2e) after sequential etching was of MWNTs. It would be impossible for the acid-treated MWNTs to stick to the silicon substrate due to the lack of any interaction of reasonable magnitude. Moreover, the MWNTs could not be dispersed in toluene as shown in Figure 1b. The presence of the polystyrene chains on the MWNT in the MWNT−PS nanocomposite is believed to be responsible for not only improving the dispersability of MWNTs in toluene as shown in Figure 1a but also the adhering of MWNTs onto the silicon substrate, resulting in a two-dimensional array.

In Figure 4a,b the bilayer structure of the MWNT−PS nanocomposite/PMMA blend film is schematically shown, along with the chemical information obtained by XPS. The C 1s peak of the freshly prepared blend surface is indicative of the carbons of the polystyrene layer. The high-resolution C 1s peak of the PS-removed (etched by cyclohexane) film includes at least three different carbon species, namely, saturated C−C, O−C=O, and C−O, which would originate from the PMMA layer lying under the top polystyrene layer. Thus, the

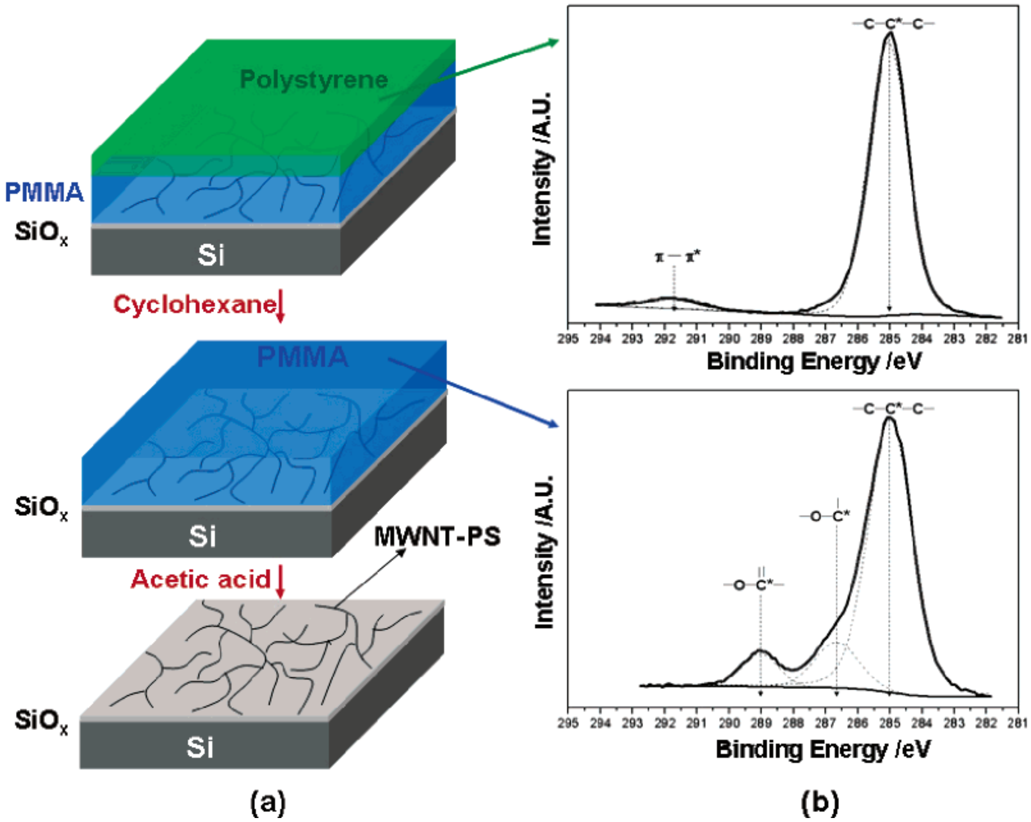

Figure 4. (a) Schematic representation of the MWNT−PS nanocomposite/PMMA (50/50, w/w) spin-cast thin films on Si wafer and (b) C 1s spectra obtained by XPS.

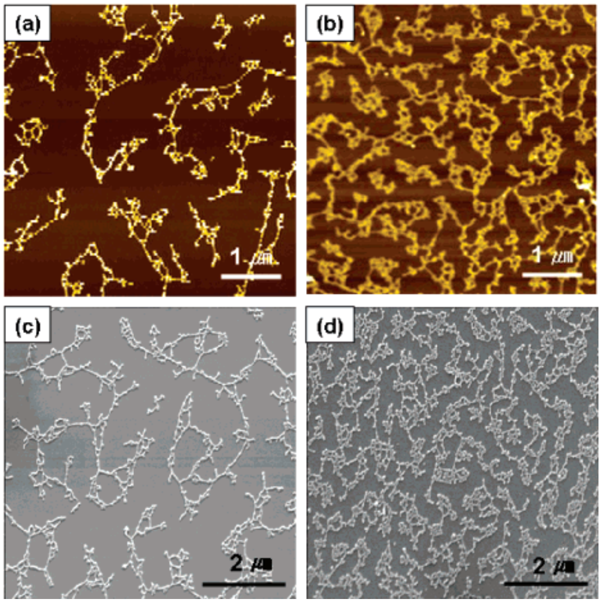

Figure 5. AFM (upper) and SEM (lower) images of the MWNT−PS nanocomposite/PMMA (50/50, w/w) spin-cast films containing different amounts of MWNT: (a, c) 0.1 wt %; (b, d) 0.5 wt %.

chemical analyses by XPS agree well with the structural observation by TEM and AFM. The effect of the MWNT concentration in the MWNT−PS nanocomposite on the formation of the nanowire array is shown in Figure 5.

The concentration was increased up to 0.5 wt %, and the nanowire array was examined by both AFM and SEM. As the MWNT concentration was increased, the density of the MWNTs formed on the substrate was increased. At 0.5 wt % most of MWNTs were found to be interconnected with each other. However, the onset of the formation of MWNT bundles of significant size, which can result in poor dispersibility, was not observed at all in the concentration range of our study.

Conclusion. MWNTs in the MWNT−polystyrene nanocomposite/PMMA blend thin film were dispersed on the silicon substrate without any aggregation and formed two-dimensional nanowire arrays. In particular, we were able to achieve these arrays of MWNTs by combining a simple spin-casting method with the phase-separation phenomenon of the immiscible polymer blend such as PS/PMMA that was facilitated by carbon nanotubes. However, MWNT arrays were not observed in both MWNT−PS nanocomposite and the PS/MWNT blend. Manipulation of these two-dimensional, random MWNT nanowire arrays can lead to many industrial applications that require deposition of carbon nanotubes such as nanoelectronic devices and functionalized coatings, etc.

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References and Notes

(1) Franklin, N. R.; Wang, Q.; Tombler, T. W.; Javey, A.; Shim, M.; Dai, H. *Appl. Phys. Lett.* **2002**, *81*, 913.
(2) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787.
(3) Tans, S. J.; Verschueren, A. R. M.; Dekker, C. *Nature (London)* **1998**, *393*, 49.
(4) Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *287*, 622.
(5) Park, S. J.; Cho, M. S.; Lim, S. T.; Choi, H. J.; Jhon, M. S. *Macromol. Rapid Commun.* **2003**, *24*, 1070.
(6) Viswanathan, G.; Chakrapani, N.; Yang, H.; Wei, B.; Chung, H.; Cho, K.; Ryu, C. Y.; Ajayan, P. M. *J. Am. Chem. Soc.* **2003**, *125*, 9258.
(7) Bandyopadhyaya, R.; Nativ-Roth, E.; Regev, O.; Yerushalmi-Rozen, R. *Nano Lett.* **2002**, *2*, 25.
(8) Shvartzman-Cohen, R.; Levi-Kalisman, Y.; Nativ-Roth, E.; Yerushalmi-Rozen, R. *Langmuir* **2004**, *20*, 6085.
(9) Chen, J.; Hannon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Ecklund, P.; Haddon, R. C. *Science* **1998**, *282*, 95.
(10) Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. *J. Am. Chem. Soc.* **2002**, *124*, 760.
(11) Dyke, C. A.; Tour, J. M. *Nano Lett.* **2003**, *3*, 1215.
(12) Baskaran, D.; Mays, J. W.; Bratcher, M. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2138.
(13) Chen, J.; Rao, A. M.; Lyuksyutov, S.; Itkis, M. E.; Hamon, M. A.; Hu, H.; Chen, Y.; Cohn, R. W.; Eklund, P. C.; Colbert, D. T.; Smalley, R. E.; Haddon, R. C. *J. Phys. Chem. B* **2001**, *105*, 2525.
(14) Zhu, J.; Yudasaka, M.; Zhang, M.; Iijima, S. *J. Phys. Chem. B* **2004**, *108*, 11317.
(15) Star, A.; Stoddart, J. F.; Steuerman, D.; Diehl, M.; Boukai, A.; Wong, E. W.; Yang, X.; Chung, S.-W.; Choi, H.; Health, J. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1721.
(16) Zorbas, V.; Ortiz-Acevedo, O.; Dalton, A. B.; Yoshida, M. M.; Dieckmann, G. R.; Draper. R. K.; Baughman, R. H.; Jose-Yacaman, M.; Musselman, I. H. *J. Am. Chem. Soc.* **2004**, *126*, 7222.
(17) Liu, J.; Rinzler, A. G.; Dai, H.; Hafner, J. H.; Bradley, R. K.; Boul, P. J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C. B.; Rodriguez-Macias, F.; Shon, Y.-S.; Lee, T. R.; Colbert, D. T.; Smalley, R. E. *Science* **1998**, *280*, 1253.
(18) Wang, H.; Zhou, W.; Ho, D. L.; Winey, K. I.; Fischer, J. E.; Glinka, C. J.; Hobbie, E. K. *Nano Lett.* **2004**, *4*, 1789.
(19) Snow, E. S.; Campbell, P. M.; Ancona, M. G.; Novak, J. P. *Appl. Phys. Lett.* **2005**, *86*, 033105.
(20) Chen, X. H.; Chen, C. S.; Chen, Q.; Cheng, F. Q.; Zhang, G.; Chen, Z. Z. *Mater. Lett.* **2002**, *57*, 734.
(21) Jia, Z.; Wang, Z.; Xu, C.; Liang, J.; Wei, B.; Wu, D.; Zhu, S. *Mater. Sci. Eng.* **1999**, *A271*, 395.
(22) Steiner, U.; Klein, J. *Phys. Rev. Lett.* **1994**, *72*, 1498.
(23) Dalnoki-Veress, K.; Forrest, J. A.; Stevens, J. R.; Dutcher, J. R. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 3017.
(24) Tanaka, K.; Takahara, A.; Kajiyama, T. *Macromolecules* **1996**, *29*, 3232.
(25) Walheim, S.; Böltau, M.; Mlynek, J.; Krausch, G.; Steiner, U. *Macromolecules* **1997**, *30*, 4995.
(26) Ton-That, C.; Shard, A. G.; Daley, R.; Bradley, R. H. *Macromolecules* **2000**, *33*, 8453.
(27) Stange, T. G.; Evans, D. F. *Langmuir* **1997**, *13*, 4459.
(28) Jacobs, K.; Herminghaus, S. *Langmuir* **1998**, *14*, 965.

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