



Low Voltage FE-SEM Examination of Organic Polymers

Application Note

Introduction

Organic polymers are a class of materials that are widely used in many traditional as well as emerging technologies. Polymers are used in applications from automotive parts, building materials, clothing, health care, battery and solar applications, and aerospace parts. Although the application range spans many levels of sophistication in materials and processing, two key factors – chemical composition and morphology – govern polymer performance. Materials science is the study of structure-property relationships via microscopy, spectroscopy, and mechanical property testing. Because morphology is a key factor to performance many microscopy techniques have been employed over the last four decades, the most ubiquitous of these is the Scanning Electron Microscope (SEM).[1]

Advances in SEM have led to brighter sources, field emission filaments; low vacuum also termed environmental SEM (eSEM), and low voltage SEM (LV-SEM). Generally samples examined in the SEM need to be electrically conducting in order to minimize charge buildup on the sample from the electron beam. Charge buildup can severely degrade the resultant image data.[1] Three approaches can be employed to minimize charging. Typically metal coat the sample with an inert metal

like gold. Another option is to increase the pressure in the sample chamber (eSEM) so that the gas molecules balance the charge. The third option is to decrease the electron beam voltage (LV-SEM) so that the beam energy is at the charge equilibrium point.

Polymers typically have low conductivity and therefore are subject to charge buildup and electron beam damage. One way to mitigate both of these issues is to use LV-SEM. However, low beam voltage operation of the SEM normally results in low resolution images.[2] In order to improve resolution and contrast in the SEM, increasing the source brightness and decreasing the initial probe size by using a field emission filament is a good solution.

Agilent's 8500 FE-SEM is a low voltage, field emission SEM which employs a novel electrostatic lens design. This innovative design allows for high resolution imaging of polymers, typically without the need for metal coating. The 8500 FE-SEM was used to image the following types of polymers, crystalline TTF-TCNQ (Tetrathiafulvalene-Tetracyanoquinodimethane, crystallized as a one-dimensional polymer), thin PTFE (polytetrafluoroethylene) films, non-woven fabric, membranes, and latex spheres.



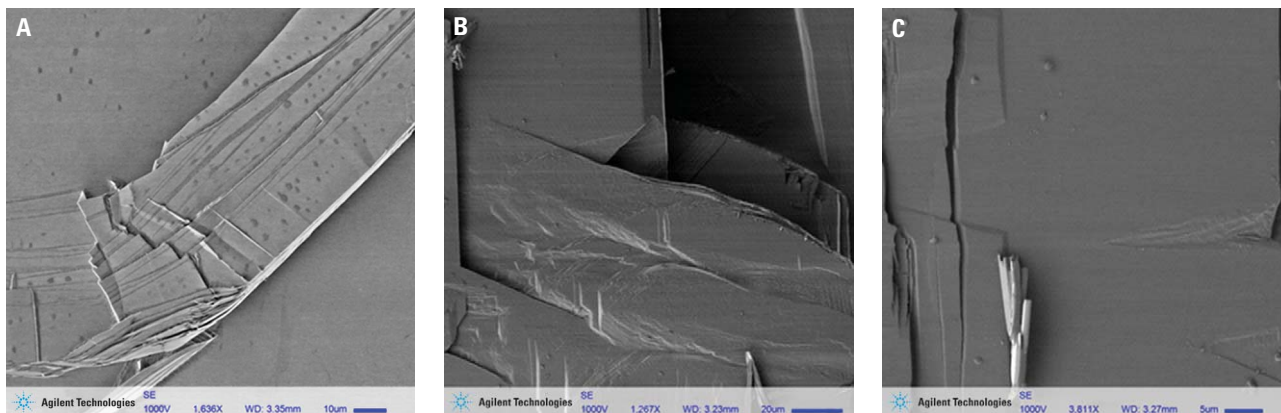


Figure 1A–C. TTF-TCNQ crystals were prepared on a freshly cleaved HOPG (highly oriented pyrolytic graphite) substrate. A–C show images of the differing surface morphologies.

TTF-TCNQ and PTFE

In order to demonstrate the utility of low voltage FE-SEM imaging of polymers, two distinctly different classes of materials were chosen. TTF-TCNQ is a crystalline pseudo one-dimensional polymer which was the first material described as an “organic metal” and therefore a good conductor.[3, 4] TTF-TCNQ was compared to PTFE, a perfluorinated polymer and a good dielectric. Each of these materials was prepared on a conducting substrate, HOPG in the case of TTF-TCNQ (Figure 1) and doped silicon in the case of PTFE (Figure 2). However in order to best demonstrate the capabilities of LV

FE-SEM imaging, one sample of doped silicon was first coated with a block copolymer before applying the PTFE film (Figure 3).

The various surface morphologies of the rod-like crystals are shown in (Figure 1A–C). Oriented nanoscale strands and thin films of PTFE can be deposited on hard substrates by unidirectional rubbing with a small diameter PTFE rod, much like drawing a line with a pencil. Figure 2 shows oriented PTFE strands produced by the rubbing process. To further demonstrate the mitigation of charge buildup by using LV FE-SEM, a block copolymer was

deposited on a silicon substrate by spin-coating and then rubbed with a small diameter PTFE rod as shown in Figure 3. The cracks in the block copolymer film were likely caused by the mechanical force of rubbing the PTFE rod. Bands of PTFE can clearly be seen in Figure 3, with the serendipitous capture of the PTFE being stretched across the surface crack in the block copolymer. No charge buildup was observed at an accelerating voltage of 1kV even in the PTFE material suspended across the cracks in the underlying material. Also no electron beam damage was observed on the nanoscale PTFE filaments that were formed by mechanical stretching across the surface cracks.

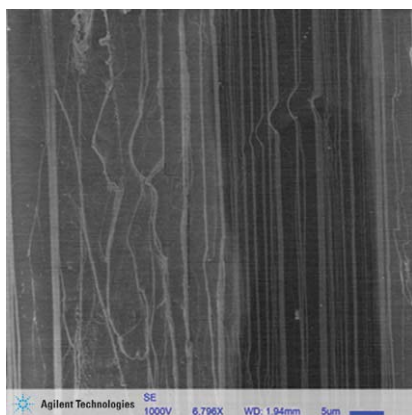


Figure 2. A narrow gauge PTFE rod was scratched unidirectional across a silicon wafer substrate. The resulting oriented polymer residue was imaged.

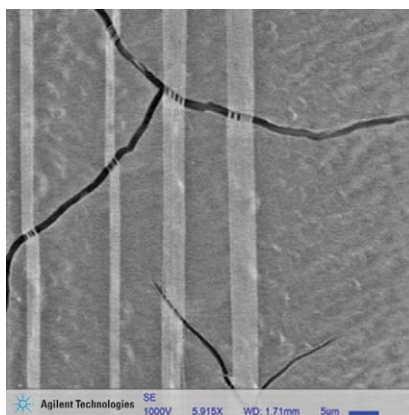


Figure 3. Similarly a narrow gauge PTFE rod was scratched unidirectional across a block copolymer film on a silicon wafer substrate. The resulting oriented polymer residue was imaged.

Non-woven Fabric

Non-woven fabrics are flat, porous sheets that are made directly from separate fibers or from molten plastic or plastic films. They are not made by weaving or knitting and do not require converting the fibers to yarn.[5]

Nonwoven fabrics are engineered fabrics that may be a single-use consumable or a very durable long-lasting product. Nonwoven fabrics provide specific functions such as absorbency, liquid repellency, resilience, stretch, softness, strength, flame retardancy, washability, cushioning,

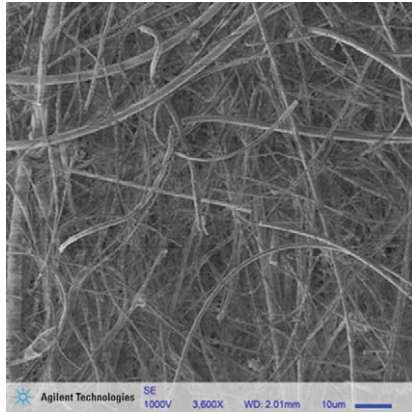


Figure 4. Non-woven fabric used in a protective face mask.

filtering, bacterial barrier and sterility. These properties are often combined to create fabrics suited for specific jobs, while achieving a good balance between product use-life and cost. They can mimic the appearance, texture and strength of a woven fabric. In combination with other materials they provide a spectrum of products with diverse range of properties, and are used alone or as components of apparel, home furnishings, health care, industrial and consumer goods.

Two easily recognizable products made from non-woven fabrics are facemasks for particle filtration and protective

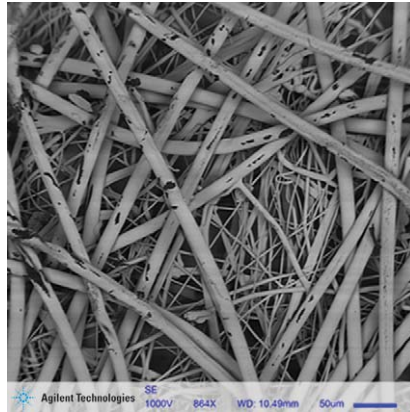


Figure 5. Non-woven fabric used in a protective outerwear garment.

outerwear worn in clean rooms or hospital operating rooms. One of the challenging aspects of imaging these fabrics with the SEM is charge buildup because the fibers used are often nonconducting. Figure 4 shows non-woven fabric from a protective face mask. A wide range of fiber diameters as well as orientations is observed. This morphology is optimized to trap small particulates. Figure 5 shows non-woven fabric from a protective garment. The morphology seen in Figure 5 is quite different than that seen in Figure 4 as the application has different requirements for physical and mechanical properties. Under LV

FE-SEM imaging conditions the samples could be examined without charge buildup.

Membranes

A polymer membrane is a thin layer of polymeric material that acts as a barrier permitting mass transport of selected species. Polymer membranes play important roles in water filtration, air quality monitoring, medical, battery and fuel cells. Two application areas garnering recent interest are air quality monitoring and green energy, specifically battery research.[6]

Air quality is a concern worldwide due to its known impact on health and environmental issues. Globally, government regulators set standards to control pollution in the air we breathe. The ability to image these polymeric membranes without the need for metal coating is important in identifying the specific particle morphology and how they are sequestered by these membranes. Figure 6 show a track etched polycarbonate membrane with an 8µm pore size. In Figure 7 we see a 0.5µm pore size track etched polycarbonate membrane. Figures 7 and 8 also show a variety of environmental particles collected on this membrane.

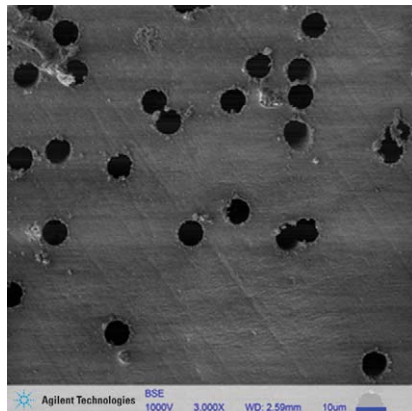


Figure 6. 8 µm track etched polycarbonate air quality monitoring membrane.

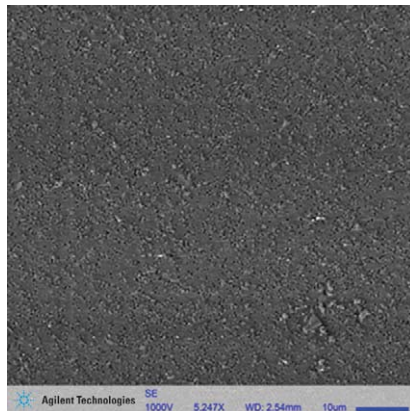


Figure 7. 0.5 µm track etched polycarbonate air quality monitoring membrane.

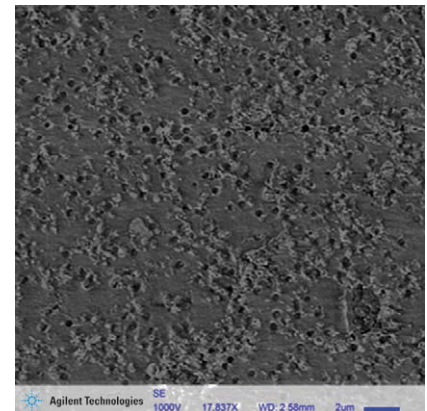


Figure 8. 0.5 µm track etched polycarbonate air quality monitoring membrane.

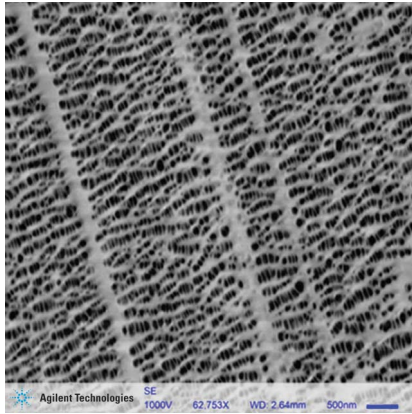


Figure 9. Celgard 2325 Lithium ion battery separator membrane.

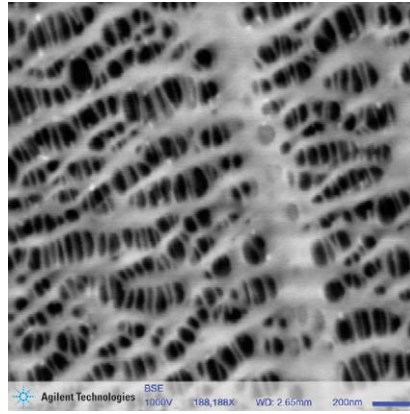


Figure 10. Celgard 2325 Lithium ion battery separator membrane.

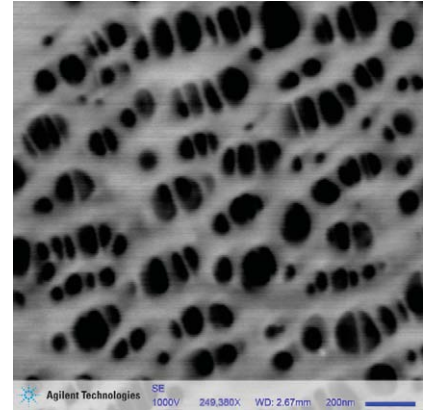


Figure 11. Celgard 2325 Lithium ion battery separator membrane.

A lithium-ion battery (Li-ion) is a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge, and back when charging. Lithium-ion electrochemical cells use intercalated lithium compounds as the electrode material instead of metallic lithium.

Lithium-ion batteries are common in consumer electronics. They are one of the most popular types of rechargeable battery for portable electronics, with one of the best energy densities, no memory effect, and a slow loss of charge when not in use. The structural and physiochemical properties of the separator membrane material strongly influence the overall cell performance, although the separator does not “actively” participate in the battery operation. A critical functional separator property is its permeability, as the presence of a solid separator material significantly increases the effective resistance of the ion-conducting electrolyte. These separators are based on polyolefin materials, such as polyethylene, polypropylene, or blends of the two. The chemical composition

and morphology attributes of the separator material significantly impact the optimization of the properties and performance characteristics. The surface morphology of Celgard 2325 was examined via LV FE-SEM (see Figures 9–11). The small pore structure created by the fibrous network is shown with increasing detail in consecutive images taken at decreasing field size (increasing magnification). The nano-scale fibers, approximately 25 nm in diameter which are clearly seen in Figure 11, govern the morphology of the pore network and therefore the performance of the membrane.

Polymer Beads and Latex Spheres

Another common polymer material is toner. Toner is a powder used in laser printers and photocopiers to form printed text and images on paper. In its early form it was simply carbon black powder. Then, to improve the quality and resolution of the printout, the carbon was melt-mixed with a polymer. Toner particles are melted by the heat of the fuser, and bind to the paper. Figure 12A–B shows an example of toner particle morphology and size distribution. Understanding the morphology, size distribution, and how these particles aggregate allows improvements to the toner properties and performance.

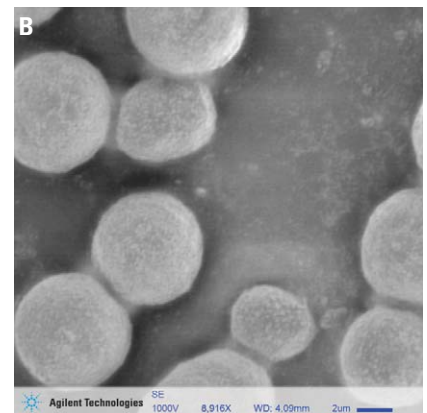
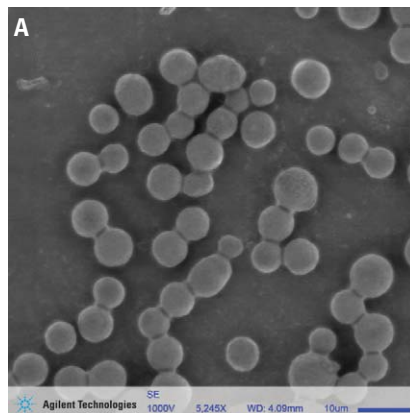


Figure 12A–B. Black dry toner particles.

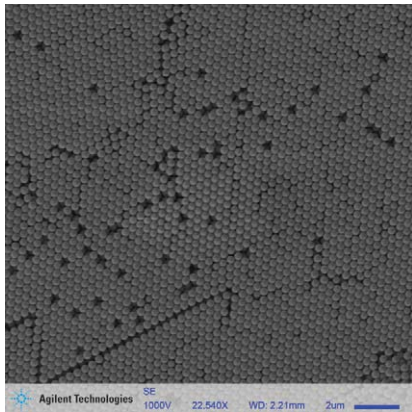


Figure 13. NIST 400 nm polystyrene bead particle standard deposited on silicon substrate by spin coating.

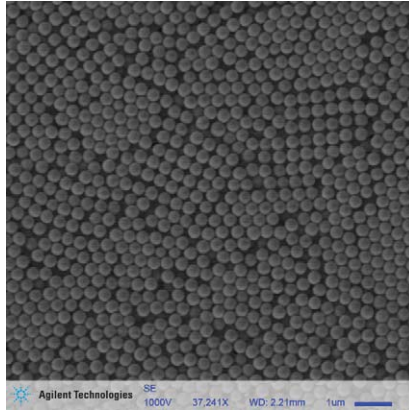


Figure 14. NIST 400 nm polystyrene bead particle standard deposited on silicon substrate by spin coating.

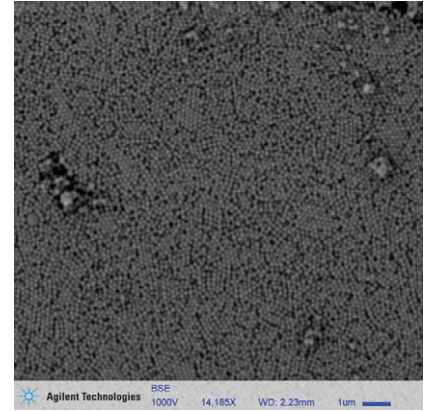


Figure 15. NIST 100 nm polystyrene bead particle standard deposited on silicon substrate by spin coating.

One of the most common polymer sphere or bead is polystyrene. Polystyrene microspheres are used in many applications, including lateral flow tests, flow cytometry, cell sorting, immuno-precipitation, fluorescence microscopy, nanosphere lithography, and as calibration particles. The microspheres are generally made by emulsion polymerization using different types of surfactants which usually are negatively charged. Once adsorbed onto the surface of the microspheres, those surfactants induce an increased colloidal stability.[7] There are two

common methods for preparing semi-crystalline arrays of polystyrene beads on substrates. One is spin coating, where the substrate is rotated at a constant rate and a suspension of the beads is added drop wise to the center of the substrate.[8] The other is solvent casting, where a small volume (typically 5–10 uL) is pipetted to the center of the substrate and allowed to slowly evaporate.

Three different sizes of monodisperse polystyrene nanospheres, 400 nm, 100 nm, and 40 nm were deposited

onto silicon substrates by spin coating (see Figures 13–21). The 400 nm nanospheres form the most dense, well packed arrays that adopt either the hexagonal or square Bravais lattice structures. As seen in Figure 13, the most common configuration is the hexagonal lattice. Figure 14 shows some of the minor configuration of the square lattice. The 100 nm nanospheres also form hexagonal and square lattices but the domain size is smaller and has more defects than the 400 nm nanospheres (see Figures 15–18). The 40 nm nanospheres

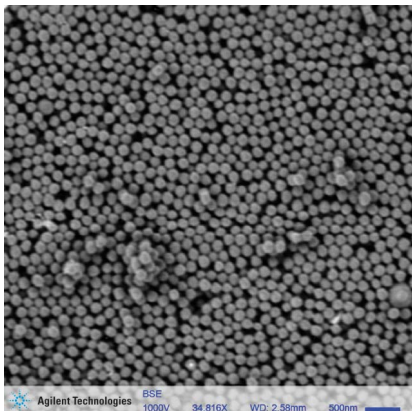


Figure 16. NIST 100 nm polystyrene bead particle standard deposited on silicon substrate by spin coating.

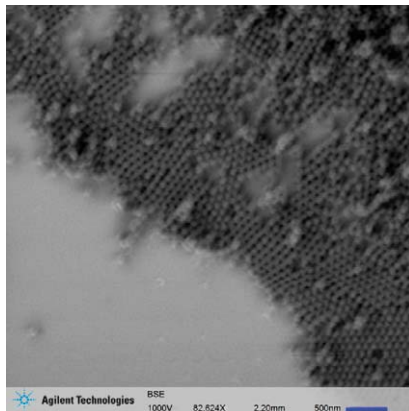


Figure 17. 100 nm polystyrene bead particle standard deposited on silicon substrate by drop casting.

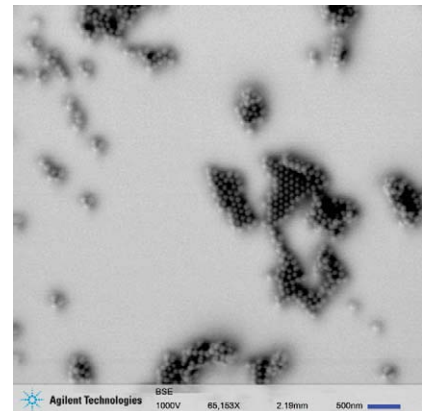


Figure 18. 100 nm polystyrene bead particle standard deposited on silicon substrate by drop casting.

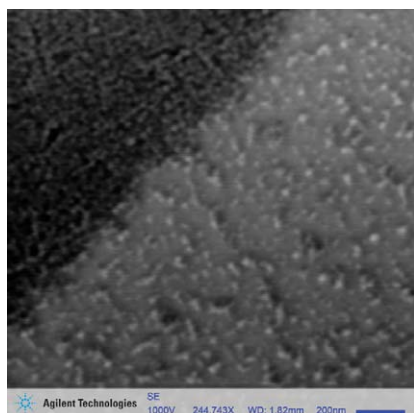


Figure 19. NIST 40 nm polystyrene bead particle standard deposited on silicon substrate by spin coating.

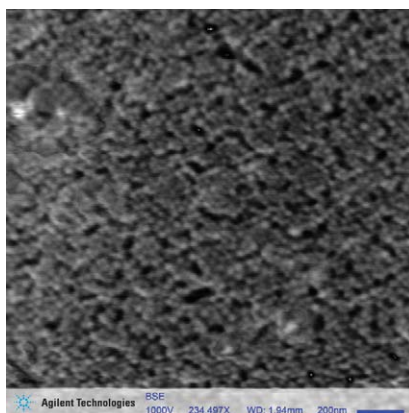


Figure 20. NIST 40 nm polystyrene bead particle standard deposited on silicon substrate by spin coating.

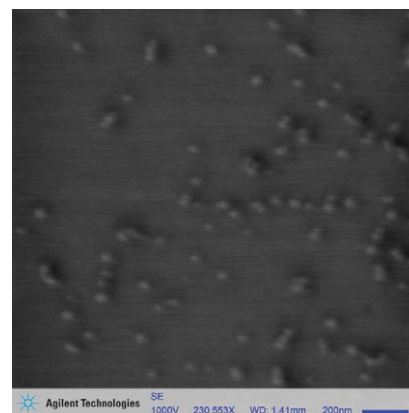


Figure 21. NIST 40 nm polystyrene bead particle standard deposited on silicon substrate by spin coating.

exhibited different behavior from the 400nm and 100 nm spheres (see Figures 19–21). As seen in Figure 19, the 40nm nanospheres form two distinct regions on the substrate, one a highly aggregated but disorganized region of spheres (Figure 20), and the other dispersed, discrete nanospheres (Figure 21). Although there are small clusters of 40 nm nanospheres in the highly aggregated region (see Figure 20) there is no discernible lattice packing structure. Figure 21 shows a region of discrete 40 nm nanospheres and their measured diameters match the

expected certified diameter. Systematic variations in sample preparation were tried with the 40nm beads, solvent casting of 1% solution, solvent casting from dilute solution 0.1%, spin coating at 150 and 300 rpm from both 1% and 0.1% solutions all yielded the same final morphology as seen in Figure 19–21. One possible explanation for the differences observed with the 40nm bead is the surface area to volume ratio (see Table 1) and how the inherent surface charges on the beads are balance versus the energetics of forming a well-ordered lattice.

Conclusions

LV FE-SEM provides a straightforward technique for high resolution imaging of polymers, typically without the need for metal coating. Although the application range of polymers examined spans many levels of sophistication in materials and processing, the morphological features of interest could easily be investigated with the Agilent 8500 FE-SEM. The primary focus of this work was on the range of materials that could be imaged with LV FE-SEM, however, the discovery that polystyrene nanospheres adopt crystalline lattice structures when they are 100nm and larger and do not when they are smaller than 100 nm was unexpected and deserves further study.

PS bead diameter in nm	Surface Area in nm ²	Volume in nm ³	Surface Area/Volume
400	502655	33510322	0.015
100	31416	523599	0.060
40	5027	33510	0.150

Table 1. Surface area, volume, and surface area to volume ratio for poly styrene nano beads.

References

1. L. Sawyer, D.T. Grubb, G.F. Meyers, Polymer Microscopy, 3rd ed., Springer, 2008.
2. J.R. Michael, D.C. Joy, B.J. Griffin, Microsc. Microanal. 15(Suppl 2).
3. U. Schwingenschl, R. Claessen, M. Dressel, C.S. Jacobsen, Phys. Rev. B 67, 125402 (2003).
4. J. Lv, H. Liu, Y. Li, Pure Appl. Chem., Vol. 80, No. 3, pp. 639–658, 2008.
5. E. Ghassemieh, M. Acar, H. Versteeg, Proc. Instn. Mech. Engrs. Vol. 216 Part L: J Materials: Design and Applications.
6. M. Ulbricht, Polymer 47 (2006) 2217–2262.
7. W. Chen, S. Tan, Z. Huang, T-K. Ng, W.T. Ford, P. Tong, Phys. Rev. E 74, 021406 (2006).
8. Y. Kadomae, M. Sugimoto, T. Taniguchi, K. Koyama, The Polymer Processing Society 23rd Annual Meeting.

Nanomeasurement Systems from Agilent Technologies

Agilent Technologies, the premier measurement company, offers high precision instruments for nanoscience research in academia and industry. Exceptional worldwide support is provided by experienced application scientists and technical service personnel. Agilent's leading-edge R&D laboratories ensure the continued, timely introduction and optimization of innovative, easy-to-use nanomeasurement system technologies.

www.agilent.com/find/nano

Americas

Canada	(877) 894 4414
Latin America	305 269 7500
United States	(800) 829 4444

Asia Pacific

Australia	1 800 629 485
China	800 810 0189
Hong Kong	800 938 693
India	1 800 112 929
Japan	0120 (421) 345
Korea	080 769 0800
Malaysia	1 800 888 848
Singapore	1 800 375 8100
Taiwan	0800 047 866
Thailand	1 800 226 008

Europe & Middle East

Austria	43 (0) 1 360 277 1571
Belgium	32 (0) 2 404 93 40
Denmark	45 70 13 15 15
Finland	358 (0) 10 855 2100
France	0825 010 700*
	*0.125 €/minute
Germany	49 (0) 7031 464 6333
Ireland	1890 924 204
Israel	972-3-9288-504/544
Italy	39 02 92 60 8484
Netherlands	31 (0) 20 547 2111
Spain	34 (91) 631 3300
Sweden	0200-88 22 55
Switzerland	0800 80 53 53
United Kingdom	44 (0) 118 9276201

Other European Countries:

www.agilent.com/find/contactus

Product specifications and descriptions in this document subject to change without notice.

© Agilent Technologies, Inc. 2011
Printed in USA, August 24, 2011
5990-8931EN



Agilent Technologies