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Atomic force microscopy of thin triblock copolymer films

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We report the elucidation of the surface morphology of a number of ABA triblock copolymers by atomic force microscopy (AFM). The chemical nature of the different phases observed in the image and the size of the respective domains was determined by image analysis. In this way the various features of the domain structure could be quantitatively determined and related to theory.

(Keywords: atomic force microscopy; block copolymer; morphology)

Introduction

The morphology of triblock copolymers is an important factor in the determination of the mechanical properties of these materials. The two component blocks segregate into different phases with a typical microdomain structure. Depending on the respective block molecular weights, their ratio, the temperature and other factors, these microdomains have a number of distinctly different forms, such as spheres, cylinders or lamellae[1]. Determination of the exact chemical nature, size and orientation of these domains is indispensible in understanding structure–property relations of the materials. Several techniques are, in principle, available to this end, of which transmission electron microscopy (TEM) is most often used. In this case, however, it is necessary to stain the triblock copolymer samples with RuO_4 in order to get a good contrast between the different domains[2]. Moreover, very thin films are required. These are obtained either by using an ultramicrotome or by casting dilute solutions of the polymers onto a water surface. This is sometimes a complicated or even impossible task. We have therefore looked into the capabilities offered by alternative techniques.

Recently, atomic force microscopy (AFM) has been applied to the study of the surface morphology of diblock copolymers[3–5]. In an AFM instrument, a very sharp tip attached to a cantilever is scanned across a surface, and its deflection is monitored by determining the deflection of a laser beam off the end of the cantilever. In this way the very small forces between the tip and the surface can be measured. The instrument is normally operated in the contact mode, whereby the tip always stays in contact with the sample during scanning. However, in the case of soft materials, such as elastomers, this often leads to sample distortion. In order to prevent this unwanted effect, the so-called tapping mode† was developed; in this mode the cantilever is vibrated at its resonance frequency and only touches the surface very lightly and very briefly. Interaction with surface features leads to a modulation of both the absolute value of the resonance frequency and its amplitude, and the surface morphology is monitored by keeping this amplitude or frequency shift at a constant value. In this mode the sample is not influenced by the tip, because there is no physical contact between tip and surface during lateral tip movements. This technique has been tried on a number of experimental styrenic triblock thermoplastic elastomers.

Experimental

All AFM images were recorded with a Nanoscope III from Digital Instruments, operated in the tapping mode in air using microfabricated cantilevers with a spring constant of $30\,N\,m^{-1}$. For analysis of the observed surface structures the Nanoscope image processing software was used. The images presented here have been corrected for sample tilt and Fourier filtered to remove low frequency noise.

The styrenic triblock copolymers were synthesized by anionic polymerization. The following experimental polymers were studied:

(A) styrene–butadiene–styrene with block molecular weights of 7.2, 34 and $7.2\,kg\,mol^{-1}$, respectively;
(B) styrene–butadiene–styrene with block molecular weights of 10, 46 and $10\,kg\,mol^{-1}$, respectively (the polybutadiene midblocks of polymers A and B had a 1,2-vinyl content of 40%. Both polymers were subsequently fully hydrogenated with a proprietary catalyst. The chemical structure of polymers A and B is therefore designated as styrene–ethene/butene–styrene copolymer);
(C) Cariflex TR 1107, a commercial styrene–isoprene–styrene copolymer with a polystyrene content of about 15% (obtained from Shell Chemicals).

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† Tapping Mode is a trademark of Digital Instruments (patent pending)

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All samples were prepared by spin-coating a 2–3 wt% solution in toluene onto a 50.8 mm silicon wafer at rotation speeds of 2000 rev min^{-1}. The ~200 nm thick films were imaged both directly, as obtained, and after annealing under vacuum at a temperature of ~110°C (above the glass transition temperatures of both blocks) for 1 and 2 weeks.

Results and discussion

We found that even when applying very low forces, of the order of 1 nN, the scanning action of the AFM microscope in the contact mode destroyed the surface of the polymer films. However, using the tapping mode, which is available on the Nanoscope III AFM instrument, we succeeded in obtaining images of the microdomains. *Figure 1* is a typical example of the AFM images which were obtained on all triblocks studied. It shows a 600 × 600 nm scan of the surface morphology of polymer A before annealing (*Figure 1a*) and after annealing for 1 and 2 weeks (*Figures 1b* and *c*, respectively). The colour-coded height scale is also shown. In these three images the domain structure is clear and appears to be lamellar, although a definite assignment requires further study. In order to determine the nature of the light and dark areas we have used image analysis to quantify the relative contribution of the dark component. We found values of 28.8, 28.5 and 29.7% (all ±2%) for the three images shown in *Figure 1*, which is in reasonable agreement with the volume fraction of polystyrene (26±1%). Therefore, we attribute the dark areas to polystyrene and the lighter ones to the midblock (rubbery) material. A similar assignment was found to be valid in all other samples studied. The effect of annealing can be seen in a better developed domain structure and higher height contrast. At this point we can only speculate about the origin of the apparent height differences observed in

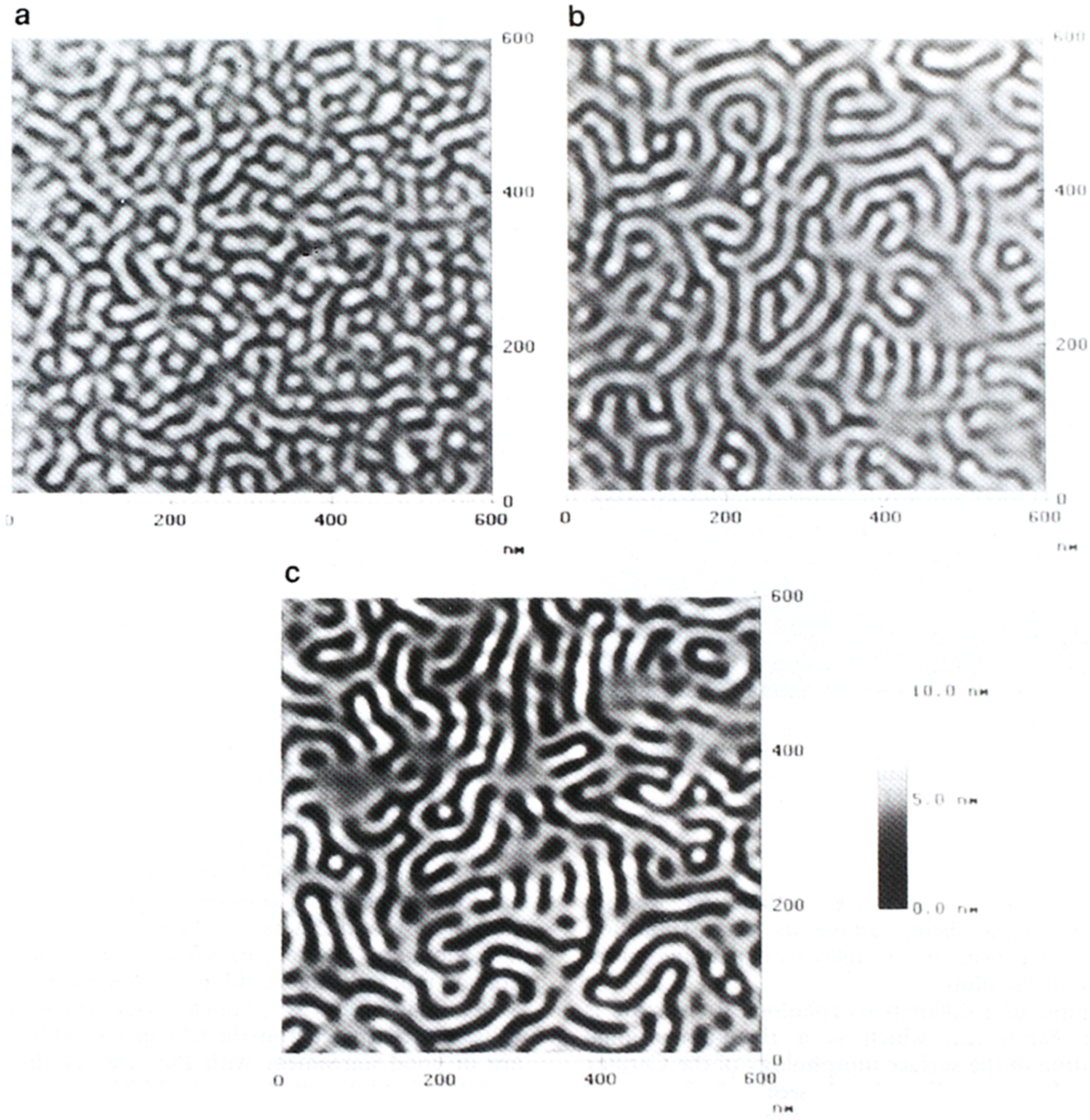

Figure 1 AFM image of the surface morphology of triblock copolymer A before annealing (a) and after annealing for 1 (b) and 2 (c) weeks. The dark structures represent the styrene component. Annealing leads to a better developed domain structure

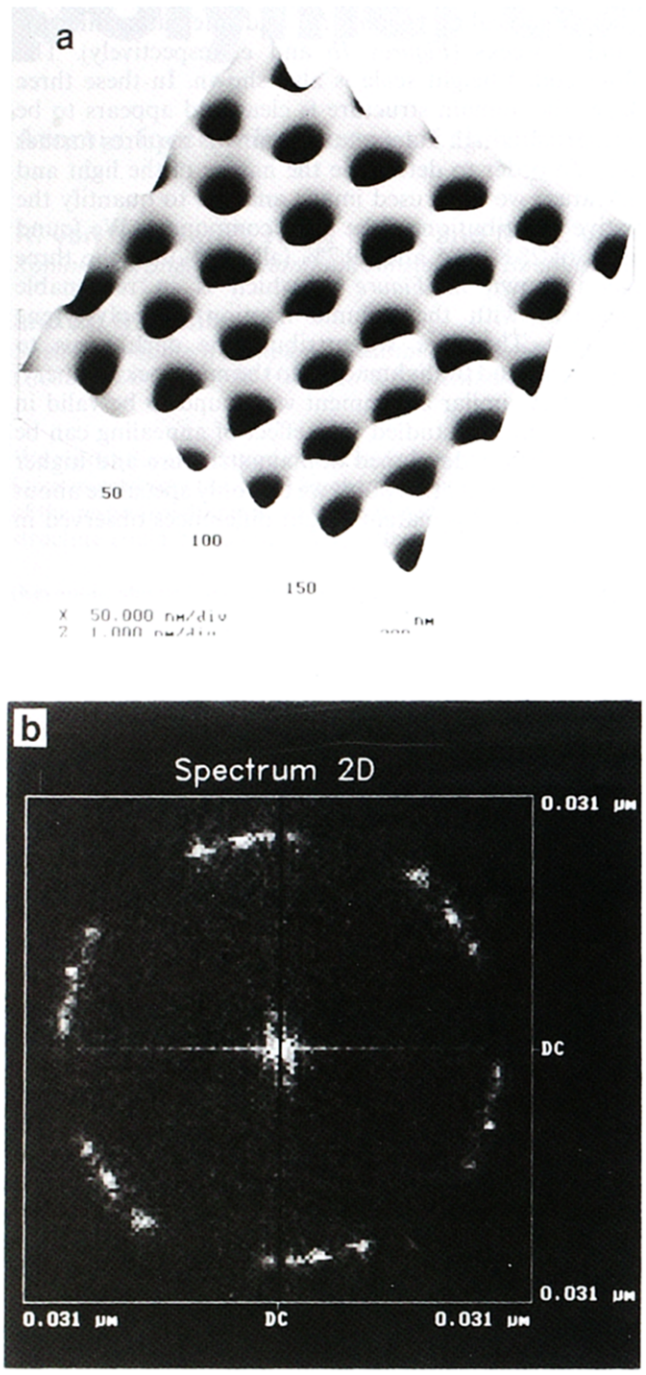

Figure 2 (a) Three-dimensional representation of the spherical morphology of the Cariflex TR 1107 triblock copolymer after annealing for 1 week. A regular hexagonal lattice is obtained, which can also be seen from the two-dimensional *FFT* (b)

the AFM images. A possible explanation is that the rubbery phase, being above its glass transition temperature, has been able to relax by expanding out of the surface of the film.

An example of a different morphological structure is shown in *Figure 2a*, which is a three-dimensional representation of the surface morphology of the Cariflex TR 1107 after annealing for 1 week. A hexagonal array of circular polystyrene microdomains was found, although some disorder is also still present. This is in agreement with TEM results obtained on the same polymer[6]. The difference in surface morphology between this triblock and that of polymer A (*Figure 1*) is directly related to the differences in polystyrene content (15 *versus* 30 wt%, respectively). *Figure 2b* shows the two-dimensional fast Fourier transform (*FFT*) of this image, which clearly confirms the hexagonal lattice. *Figure 3* shows two *FFT* spectra of polymer A (*Figure 1*) and of polymer B. A comparison of these *FFT* images clearly shows that there is a difference in the size of the microdomains in the two samples. The characteristic domain repeat distances obtained from these images were 31 ± 2 nm for A and 37 ± 2 nm for B (minimum/maximum values as determined from the *FFT* spectrum). These values are in good agreement with the sizes of the domains as determined directly from the AFM images (14.7 ± 0.9 and 18.5 ± 0.9 nm for the styrene domains and 16.3 ± 0.9 and 18.7 ± 0.9 nm for the rubbery domains for polymers A and B, respectively). According to theory[7], the diameter,

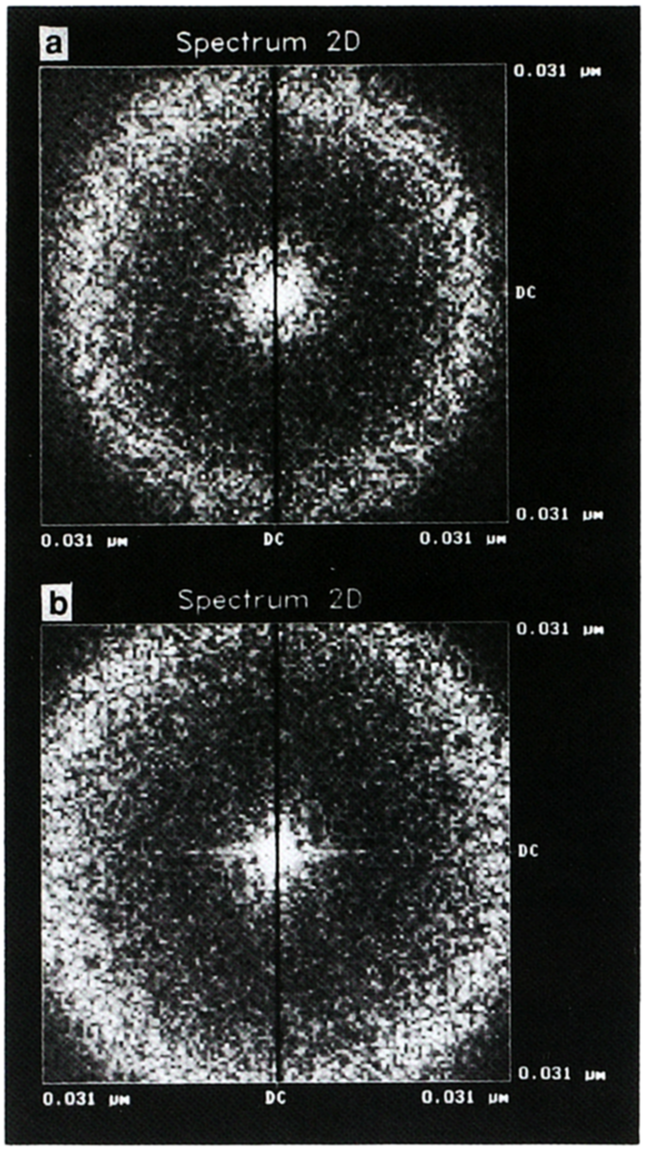

Figure 3 Two-dimensional *FFT* spectra of triblock copolymers A (a) and B (b). From a comparison of these *FFT* spectra a clear difference in the characteristic length scale can be seen and also quantitatively determined (see text)

D, of the polystyrene domains scales with the block molecular weight, *M*, as $D = M^{\alpha}$. For polymers A and B we thus obtain a value of $\alpha = 0.68 \pm 0.24$, which is in very good agreement with theoretical predictions[7]. It should be noted, however, that this value is based on a limited data range in molecular weight.

Conclusion

We have been able to image the surface morphology of a number of triblock copolymers with AFM in the tapping mode. Using image analysis we could determine the chemical nature of the different phases observed in the images. Furthermore, the size of the different domains could be determined and related to theory.

References

1 Folkes, M. J. and Keller, A. in 'Block and Graft Copolymers' (Eds J. J. Burke and V. Weiss), Syracuse University Press, New York, 1973
2 Yamaoka, I. and Kimura, M. *Polymer* 1993, **34**, 4399
3 Cai, Z., Huang, K., Montano, P. A., Russell, T. P., Bai, J. M. and Zajac, G. W. *J. Chem. Phys.* 1993, **98**, 2376
4 Annis, B. K., Schwark, D. W., Reffner, J. R., Thomas, E. L. and Wunderlich, B. *Makromol. Chem.* 1992, **193**, 2589
5 Collin, B., Chatenay, D., Coulon, G., Ausserre, D. and Galot, Y. *Macromolecules* 1992, **25**, 1621
6 Han, C. D., Kim, J. and Kim, J. K. *Macromolecules* 1989, **22**, 383
7 Helfand, E. and Wasserman, Z. R. *Macromolecules* 1976, **9**, 879