New techniques for determining domain morphologies in block copolymers

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We have developed several new techniques for examining the domain morphologies of microphase-separated block copolymers. By selective degradation and removal of the matrix component of suitable block copolymers, the domain-forming component can be left intact in its original morphological form and available for characterization. Thus we have selectively removed the polydiene (polybutadiene or polyisoprene) matrix component of poly(styrene-*b*-diene) copolymers by treatment with ozone. The remaining polystyrene domains were stained with ruthenium tetroxide or shadowed with platinum and examined by electron microscopy. A marked improvement in the ability to distinguish domain morphologies and their three-dimensional character was found when these degradation techniques were used. Details of domain morphologies that were not apparent when using conventional osmium tetroxide staining methods on undegraded films often became clearly apparent with this new technique.

(**Keywords: block copolymer; morphology; micelles; ozone degradation; staining; electron microscopy**)

INTRODUCTION

Microphase separation often occurs in the simple A–B and A–B–A block copolymers and results in the development of very regular domain morphologies. The study of these domain morphologies, their relationship to properties and the theory for formation have been the subject of numerous publications in the past several decades, following the pioneering work[1] of Sadron, Skoulios and their associates at the (now) Institut Charles Sadron in Strasbourg. Since the domains in di- and triblock copolymers have dimensions that are typically in the range of 100–500 Å, investigation of domain morphologies has depended on the use of transmission electron microscopy (TEM). This requires the use of ultra-thin specimens, with the result that whatever morphology exists in the specimen is shown in a two-dimensional view, and often giving a misleading impression of the exact nature of the domain morphology. For example, a system having a cylindrical domain morphology can appear to have a spherical or a lamellar morphology if the cylindrical domains are oriented normal or parallel, respectively, to the plane of the film[2]. Although some information about the three-dimensional character of the structure can be obtained by tilting the specimen stage in the electron microscope[3], the information is limited to small-scale effects. Very little information about the large-scale three-dimensional character of the morphology has been available. The three-dimensional character of the domain morphology obviously affects many physical properties (mechanical, diffusional, etc.) of block copolymers. If the relationships between morphology and properties are to be understood, it is necessary to know more about the three-dimensional character of a domain morphology, e.g. the length and orientation of cylindrical domains, the lateral extent of lamellar domains, the deformation of the domain morphology under stress, etc. This paper describes experimental techniques by which new information about the domain morphology of a block copolymer and its three-dimensional character can be obtained.

The techniques we have developed to provide additional information about domain morphologies are based upon the selective removal of one of the components of a microphase-separated block copolymer, leaving the other component intact and still retaining the morphological form it had in the microphase-separated state. The details of the domain morphology of that component can then be examined by electron microscopy. Thus, polystyrene domains have been isolated from the polydiene matrix component of poly(styrene-*b*-butadiene) (S–B) or poly(styrene-*b*-isoprene) (S–I) block copolymers by selective degradation and removal of the diene component with ozone. Each double bond of the diene chains is rapidly cleaved by ozone[4] and converted into low-molecular-weight compounds, which are eliminated by evaporation or dissolution. The polystyrene domains are unaffected by ozone during the short time required to remove the polydiene component and are left in the morphological form they had in the original microphase-separated system. Although we have applied such degradation techniques to block copolymers in both film form and in solution (micellar solutions), in this paper we shall limit the discussion to techniques and results for film specimens. Results for several S–B and S–I copolymers that were cast from a variety of selective and non-selective solvents will be presented here.

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EXPERIMENTAL

Exposure of the film samples to ozone was done by passing ozone into a glass dome chamber that covered the samples. The ozone was generated by an Ozone Research and Equipment Corporation (OREC) 'O'-series ozonator. It produces ozone by passing an oxygen stream through an electrical discharge, giving an ozone concentration of approximately 5% at a rated output of 10 g h^{-1}. Flow rates were monitored with flow meters, and ozone concentrations were determined by passing a measured portion of the gas stream into a potassium iodide solution. The resulting I_2 was determined by a colorimetric titration using a standard sodium thiosulphate solution with a starch end-point indicator. All equipment exposed to the ozone stream was either stainless steel, glass or Teflon. A 30 min exposure to ozone was typically sufficient to degrade completely the diene component of the thin films used, with the intact polystyrene domains left behind. The polystyrene was not degraded by ozone (as indicated by g.p.c. molecular weights), and the size of the polystyrene domains did not appear to change with exposure times.

Thin films of the various S–B and S–I block copolymers were prepared by casting dilute solutions (0.01–1%) of the polymers on a water surface or on a Formvar-coated glass slide. Evaporation of the solvent then left a very thin film of the polymer. Since the films were prepared by solvent evaporation and not annealed, they may have been in non-equilibrium states. This was not considered important for the present investigation, since the focus was to demonstrate that ozone degradation techniques offered significant advantages over existing techniques in clarifying domain morphologies.

The solvents used included selective solvents ('good' for one block component and 'bad' for the other) as well as non-selective solvents (equally 'good' for both components). Treatment of the films with ozone and recovery of the degraded films for electron microscopy was done in three different ways. First, films cast on a water surface could be treated with ozone while still floating on the water surface. The degraded diene component either evaporated or dissolved in the water, leaving the polystyrene domains floating on the surface. They were collected for examination by simply dipping a Formvar-coated TEM grid into the water and drawing it up through the surface. A second technique involved picking up a cast film on the water surface on a Formvar-coated TEM grid, and then exposing the film on the grid to ozone. This technique had the advantage of yielding a very high concentration of polystyrene domains on the grid. Stainless-steel grids were used when the grids were exposed to ozone, since it was found that the usual copper grids were attacked by ozone. In the third technique, a thin film of a polymer solution was spread on a Formvar-coated glass slide, and then treated with ozone while on the slide. After the ozone treatment, the Formvar film with the polymer film remnants on it was floated off on water and picked up on a TEM grid. This method also had the advantage of yielding high concentrations of domains. Films of the undegraded polymers were prepared for electron microscopy by casting solutions on water and then drawing a TEM grid up through the floating film. Electron micrographs of the various films were obtained using a Philips 301 Electron Microscope, with a typical accelerating voltage of 60 kV.

The undegraded films (still containing the diene component) were stained with osmium tetroxide[5] by placing the films (on their supporting TEM grids) over a 1% aqueous solution of osmium tetroxide for periods of 15–60 min. Since osmium tetroxide does not stain polystyrene, this technique obviously could not be used to examine the degraded films, which contained only polystyrene. The degraded samples, which contained only polystyrene, were stained with ruthenium tetroxide, as described by Trent *et al.*[6,7], or were shadowed with platinum. The polystyrene domains on the grids could be stained in as little as 5 min by exposure over a 0.3% aqueous solution of ruthenium tetroxide. Of course, ruthenium tetroxide could not be used to stain undegraded films since it stains both polydiene and polystyrene, and the resulting stained films would appear uniformly black. Shadowing with platinum (at a known angle for height determination) was done by evaporation of a platinum–carbon pellet in a Kinney Vacuum Evaporator.

The samples used in these investigations are shown in *Table 1*.

RESULTS AND DISCUSSION

Non-selective solvents

Figures 1 and *2* are electron micrographs of block copolymer domain morphologies shown by use of the conventional osmium tetroxide staining techniques and by use of ozone degradation with subsequent ruthenium tetroxide staining techniques. *Figure 1* shows the domain structure of SB(22-55), which had been cast as a thin film on water from a toluene solution (a 'good' and

Table 1 Details of samples used

Sample	Molecular weight Styrene	Molecular weight Diene	Code
Poly(styrene-b-butadiene)[a]	22000	55000	SB(22-55)
Poly(styrene-b-butadiene)[a]	12000	71000	SB(12-71)
Poly(styrene-b-isoprene)[b]	94000	85000	SI(94-85)

[a] From Dr J. G. Balas, Shell Development Co., Houston, Texas
[b] From Dr R. W. Richards, Durham University, Durham, UK

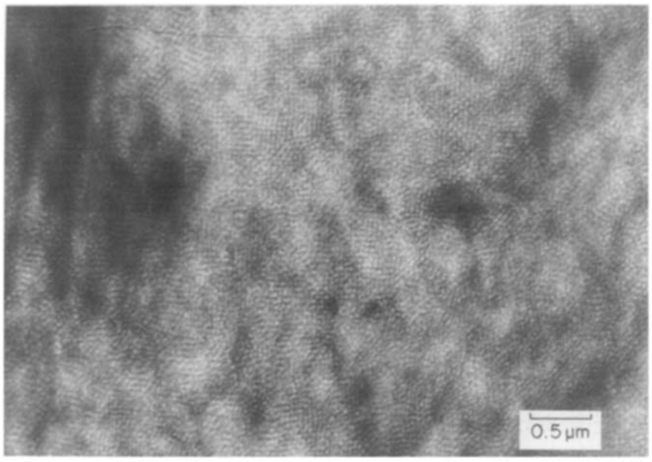

Figure 1 Electron micrograph of SB(22-55) cast on water from benzene solution and stained with osmium tetroxide

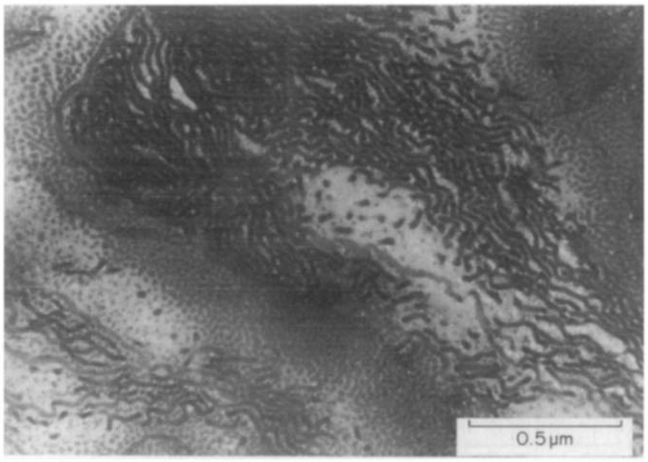

Figure 2 Electron micrograph of SB(22-55) cast on water from toluene solution, degraded with ozone and stained with ruthenium tetroxide

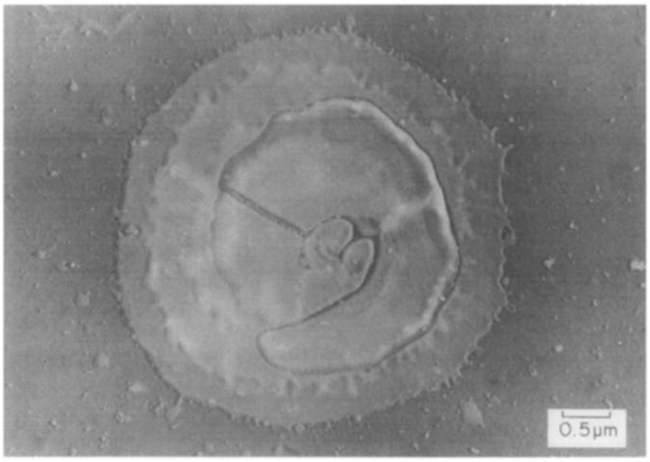

Figure 3 Electron micrograph of SI(94-85) cast on a Formvar-coated glass slide from toluene solution, degraded with ozone, stained with ruthenium tetroxide and shadowed with platinum

non-selective solvent for both block components), followed by staining of the polybutadiene component with osmium tetroxide. Although the domain morphology is not clearly defined, the micrograph does give the impression that the domains are cylindrical (as would be expected from the composition of SB(22-55))[8]. In contrast, *Figure 2* shows the results of treating the polymer film (on water) with ozone to remove the polybutadiene component, followed by staining of the remaining polystyrene domains with ruthenium tetroxide. In this micrograph, the cylindrical morphology of the polystyrene domains is obvious, as is their three-dimensional character. The cylinders have diameter of approximately 300 Å and many have lengths of over 3000 Å. The small spheres seen in *Figure 2* may be the cores of spherical micelles, but it is more likely that they are non-equilibrium entities developed during the film formation process. A comparison of *Figures 1* and *2* clearly demonstrates the power of this degradation method to clarify domain morphologies and provide information about their three-dimensional character.

Figure 3 shows the morphology of SI(94-85), which had been cast from a toluene solution on a Formvar-coated glass slide and treated with ozone. The degraded block copolymer film (on the Formvar backing) was floated off and picked up on a TEM grid, and then stained with ruthenium tetroxide and shadowed with platinum. The expected morphology of this block copolymer with its approximate 1/1 composition is lamellar[8] (when cast from a non-selective solvent), and that morphology was observed in microtomed specimens cut from a thick film (not shown here). *Figure 3* shows a tiered 'island' approximately 4.2 μm wide, with a terrace height of approximately 150 Å. It is believed that each tier is an individual polystyrene lamella. This micrograph shows that the lamellae in the cast film had lateral dimensions at least of the order of micrometres.

Selective solvents

In selective solvents ('good' for one block component and 'bad' for the other), diblock copolymers form micelles in dilute solutions. The core of the micelle is formed by the insoluble component, while cilia-like chains of soluble component project into the solvent and prevent aggregation of the micelles by a steric stabilization mechanism[9]. The formation of polymeric micellar systems has been discussed by a number of authors, and a review of such systems has been given by Price[10]. Theories for the formation have been presented by several groups, e.g. Noolandi and Hong[11], Leibler, Orland and Wheeler[12], Nagarajan and Ganesh[13] and Halperin[14]. Micelle formation in block copolymer/homopolymer blends also occurs, and has been discussed by Kinning, Thomas and Fetters[15] and Kao and Olvera de la Cruz[16].

Poly(styrene-*b*-diene) copolymers form micellar systems in solvents such as n-octane, which is a good solvent for polydienes and a poor solvent for polystyrene. We shall compare results concerning micellar properties when conventional osmium tetroxide staining is used and when ozone degradation is used, and followed by staining with ruthenium tetroxide or shadowing with platinum. *Figures 4* and *5* are electron micrographs showing films of SB(22-55) (*Figure 4*) and SI(94-85) (*Figure 5*), which were formed by casting 1% solutions in n-octane on water and then stained with osmium tetroxide. In *Figure 5*, the polystyrene micellar cores from SI(94-85) are clearly defined, while those of SB(22-55) in *Figure 4* are not. The poorer definition results from the larger

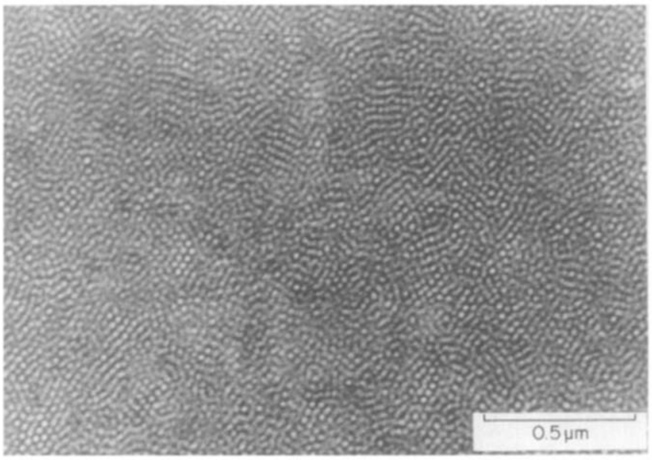

Figure 4 Electron micrograph of SB(22-55) cast on water from n-octane and stained with osmium tetroxide

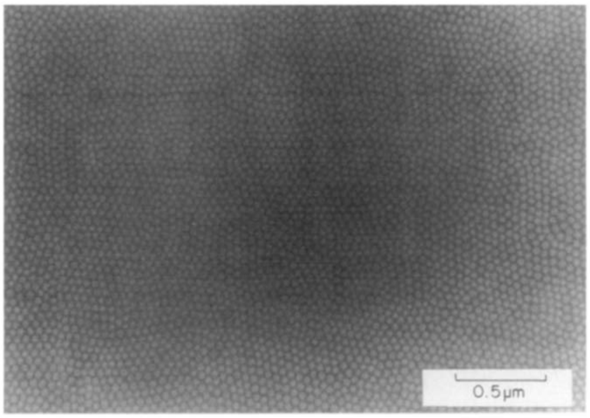

Figure 5 Electron micrograph of SI(94-85) cast on water from n-octane solution and stained with osmium tetroxide

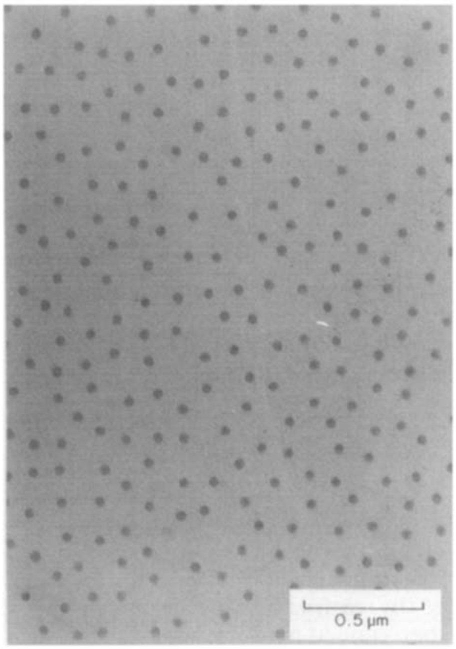

Figure 6 Electron micrograph of SB(22-55) cast on a Formvar-coated glass slide from n-octane solution and stained with osmium tetroxide

fraction of the polydiene component in SB(22-55) (where it is actually the predominant component). Such films will be stained predominantly black with osmium tetroxide, and the non-stained polystyrene micellar cores will be obscured to a degree that depends on the relative fraction of the polydiene component.

It is of interest to note the different appearance of micelles stained with osmium tetroxide when the micellar solutions have been spread on water and on glass. When spread on water (*Figures 4* and *5*), the mobility of the solution on the substrate allows the micelles to form a coherent film. When then stained with osmium tetroxide, the unstained micellar cores appear white on a black-stained polybutadiene background. In contrast, when a dilute micellar solution is spread onto glass or rigid substrate, the micelles remain isolated from one another, and, as *Figure 6* shows, the micelles appear uniformly black when stained with osmium tetroxide. The difference in the appearance of the micelles when cast on water and on a rigid substrate is an effect arising from minimization of the surface free energy of a condensed film system and of an isolated micelle. When cast on a rigid substrate, isolated SB micelles minimize their surface free energy by adopting a spherical shape, which includes an enveloping shell of polybutadiene around a central polystyrene core. The stained micelle will then appear uniformly black. In a condensed film system, the surface free energy is minimized by levelling of the film, so that the thickness of polybutadiene over the upper surface of a spherical core will be less than between the cores. Because of the thickness differences, this matrix material will appear much darker after staining than the material over the upper surfaces of the cores, so the cores will appear light on a dark background (with an apparent size that is not the true micellar core size).

Figure 7 shows micellar cores from SB(22-55), which was cast on Formvar-coated glass slides, degraded with ozone and stained with ruthenium tetroxide. The difference in size of the intact micelles (~400 Å) shown in *Figure 6* and the micellar cores (~250 Å) in *Figure 7* corresponds reasonably well with that expected from the composition of the copolymer.

Figures 8 and *9* are electron micrographs of SB(22-55) films prepared by casting 1% n-octane solutions on water and then degrading with ozone. The cores shown in *Figure 8* have been stained with ruthenium tetroxide, while those in *Figure 9* have been shadowed with platinum. The micellar cores that remain after the films are degraded on water are mobile and aggregate to form the 'rafts' seen in these figures. A comparison of *Figures 4* and *8* or *9* again shows the enhanced clarification of morphological features that results when one block component is removed. Whereas the size of the micellar cores can only be estimated in *Figure 4*, they are clearly defined and easily measured (~280 Å diameter) when they have been isolated from the matrix material and then stained.

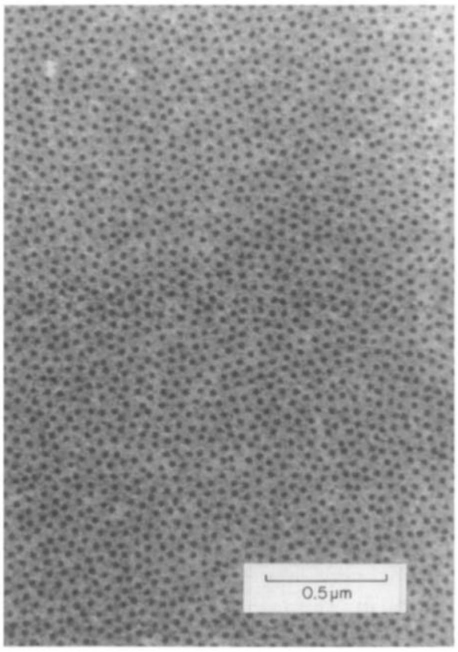

Figure 7 Electron micrograph of SB(22-55) cast on a Formvar-coated glass slide from n-octane solution, degraded with ozone and stained with ruthenium tetroxide

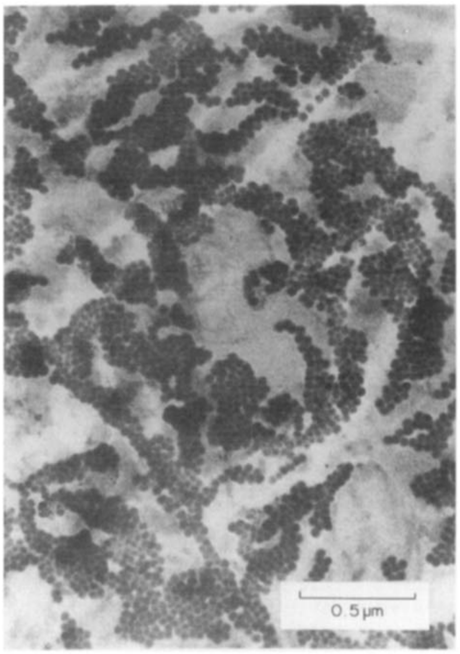

Figure 8 Electron micrograph of SB(22-55) cast on water from n-octane solution, degraded with ozone and stained with ruthenium tetroxide

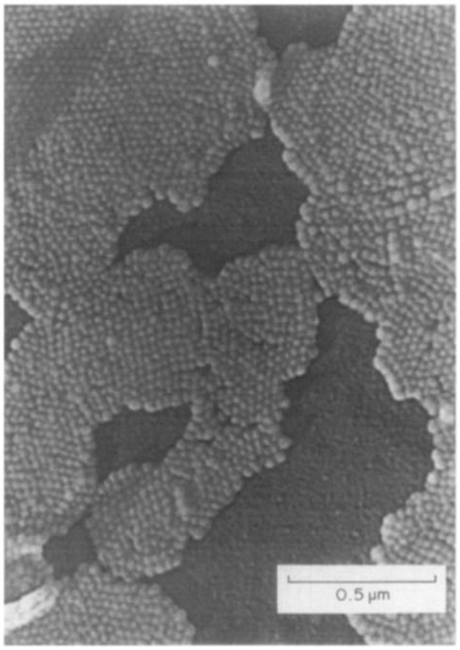

Figure 9 Electron micrograph of SB(22-55) cast on water from n-octane solution, degraded with ozone and shadowed with platinum

The cleavage of the polybutadiene chains from the micellar cores by ozone results in the formation of carboxyl groups on the micellar core surfaces. By neutralization of these groups with a base such as sodium hydroxide, the resulting ionic charges on the cores prevent aggregation of the cores through electrostatic repulsion effects. The effectiveness of these charge effects is shown by *Figure 10*, which shows isolated micellar cores of SI(94-85) resulting from ozone degradation on a dilute solution of sodium hydroxide (then picked up on a Formvar grid).

The cores shown in *Figure 10* have been shadowed with platinum, and from the shadowing angle (10°) and shadow lengths the core heights are estimated to be approximately 250 Å. This compares to the average diameter of approximately 500 Å, indicating that the cores are flattened into a somewhat oblate shape. It is not clear whether this non-spherical shape is inherent to these micelles or whether spherical cores become oblate (flatten) as a result of capillary forces during drying of the film, or as a result of heating. If heated above the glass transition temperature of polystyrene during shadowing or during examination by the electron beam, the cores could flatten by gravitational or by wetting effects. However, heating above T_g in the electron beam is considered unlikely[17], and even if it occurred a comparison of the relative energetics associated with the surface tension (tending to preserve a spherical shape) and gravity (tending to flatten the shape) shows that the surface tension effects ($2\gamma/r$) of such very small spheres would far outweigh gravitational effects ($2\rho gr$), and the cores would remain spherical even if heated above T_g (unless wetting of the surface was also involved). Most likely, the oblate shape is the result of capillary forces during film drying.

Mixed solvents

Figures 11 and *12* show the morphologies of ozone-degraded thin films of SB(22-55), which have been cast on water from solutions in a mixture of 'good' and 'bad' solvents for one or the other of the block components. These figures show two of the wide variety of polystyrene morphologies that have been noted when mixed solvents are used. The complex morphologies are apparently the result of the interplay between relative rates of solvent evaporation or solution in water of the mixed solvents and the resulting changed 'quality' of the solvent system.

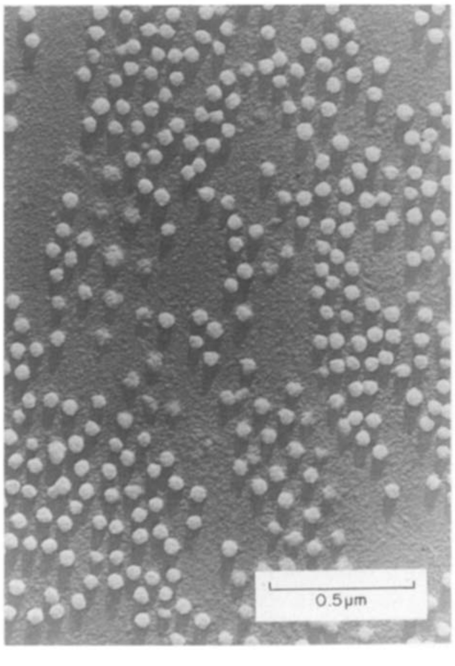

Figure 10 Electron micrograph of SI(94-85) cast on a dilute solution of sodium hydroxide from n-octane solution, degraded with ozone and shadowed with platinum

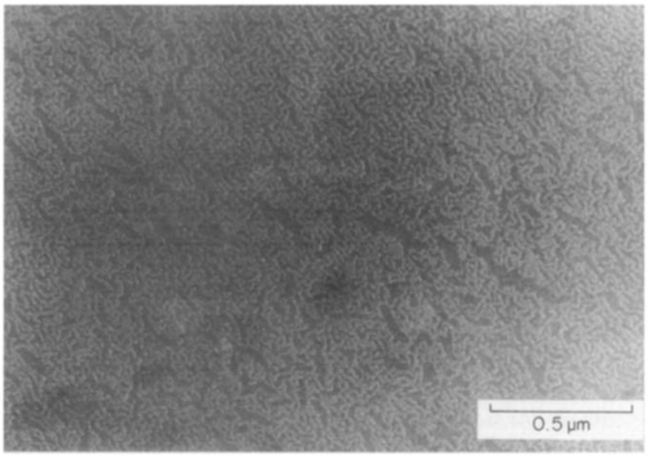

Figure 11 Electron micrograph of SB(22-55) cast on water from an 80/20 n-octane/toluene solution, degraded with ozone and shadowed with platinum

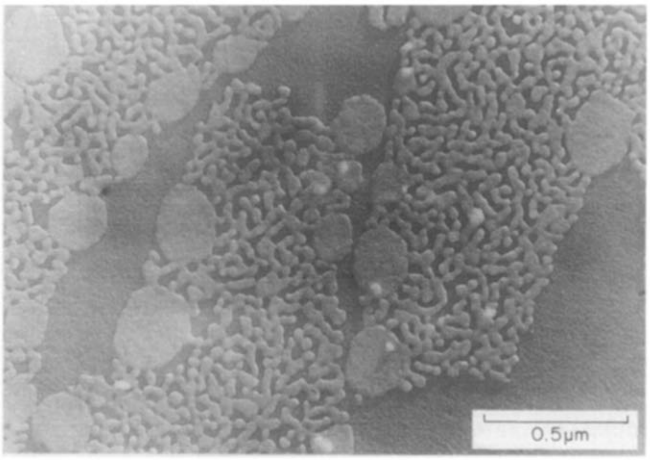

Figure 12 Electron micrograph of SB(22-55) cast on water from 60/40 methyl isobutyl ketone/n-octane solution, degraded with ozone and shadowed with platinum

CONCLUSIONS

We have shown that it is possible to remove selectively the diene component of styrene–diene block copolymers from a domain-structured system. Polystyrene domains are left intact and offer an enhanced opportunity to characterize the true three-dimensional domain morphology of such block copolymers. This has been particularly valuable for systems having a cylindrical or lamellar morphology, for which it has been possible for the first time to obtain information on the length of cylindrical domains and the lateral size of lamellar domains as they actually exist in the domain system. Although the results presented here have made use of the ozone degradation of diene polymers, the concept has general validity and, in principle, could be used for any system for which a selective degradation technique is available.

The focus of the work reported here has been the development of techniques for the characterization of the domain morphology of block copolymers, in which only microscopic quantities of the polystyrene domains are recovered and examined. However, the separated domains are of interest in other respects. Those prepared from micellar solutions are carboxy-functionalized microspheres with sizes that can be controlled in the range of 100–500 Å. Preparation of functionalized microspheres in this size range is difficult using other preparative techniques, so these degradation techniques offer opportunities for new materials and applications. We have developed techniques to produce and recover macroscopic quantities of the microspheres, and have shown that they can serve as carriers for other entities through coupling to the surface carboxylate groups. These techniques and results will be reported in a subsequent publication[18].

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