# Critical Molecular Weight for Block Copolymer Reinforcement of Interfaces in a Two-Phase Polymer Blend[†]

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ABSTRACT: The effect of a small addition of poly(styrene-*b*-2-vinylpyridine) block copolymer on the microstructure and mechanical properties of phase-separated blends of polystyrene (PS) and poly(2-vinylpyridine) (PVP) was investigated by transmission electron microscopy on thin films cast from solution. Our experiments allow us to separate the effect of the bcp addition on the morphology from its effect on the strength of the interface between the two phases. A series of block copolymers with a PS degree of polymerization > 390 and a PVP degree of polymerization varying between 68 and 570 were added to the blends. Although we expect in all cases significant segregation of the block copolymer to the interface and a corresponding decrease in the interfacial tension, only those copolymers whose PVP block degree of polymerization was above 200 were found to be effective in preventing failure at the interface. This critical value corresponds roughly to the molecular weight between entanglements $M_e$, suggesting therefore that at least one average "entanglement" between the PVP block and the PVP homopolymer is necessary to have good stress transfer at the interface.

## Introduction

It has been known for some time that additions of diblock copolymers to phase-separated blends of immiscible homopolymers could improve their mechanical properties.[1-5] Part of this improvement undoubtedly comes from the fact that such block copolymers can act as polymeric surfactants, segregating to interfaces between the two phases, thus decreasing the interfacial tension and making it easier to create smaller scale microstructures by melt processing methods. But part of this improvement also may result from the reinforcing action of the block copolymers themselves on the interface. This paper is aimed at increasing our understanding of this reinforcement by investigating, using quantitative electron microscopy, the microscopic aspects of this problem in a simple model system. With this technique we are able to separate the effects of phase size from those of the block copolymer itself. We demonstrate, in particular, that there is a minimum molecular weight the shorter diblock must have in order for it to reinforce even the interfaces of small second-phase particles.

The system we have chosen consists of the immiscible homopolymers polystyrene (PS) and poly(2-vinylpyridine) (PVP). Both polymers have about the same glass transition temperature, and because of the similarity in chain dimensions we assume that they have about the same molecular weight between entanglements as determined from values of the shear modulus on the rubbery plateau. This assumption is buttressed by the deformation behavior of these two homopolymers. Both deform plastically by crazing in preference to shear deformation. The stress for crazing appears to be similar for both PS and PVP, and the extension ratio of the craze fibrils, as determined by mass thickness contrast measurements, is the same, $\lambda = 4.0$.

Table I
Degrees of Polymerization and Polydispersity of the Block Copolymers

| dPS block | PVP block | $M_w/M_n$ |
|---|---|---|
| 391 | 68 | 1.03 |
| 1300 | 173 | 1.07 |
| 391 | 220 | 1.07 |
| 391 | 476 | 1.10 |
| **PS block** | **PVP block** | **$M_w/M_n$** |
| 480 | 90 | 1.08 |
| 570 | 570 | 1.14 |

## Experimental Section

Diblock copolymers of PS and PVP were prepared by anionic polymerization with nearly monodisperse block lengths using a cumylpotassium initiator in tetrahydrofuran. The polymerization was carried out at -55 °C. The characteristics of the resulting diblock copolymers are shown in Table I. Some of these block copolymers were prepared with a deuterated polystyrene block in order to allow their use as markers in a forward recoil spectrometry experiment done in a separate study.[6] The diblock copolymers will be designated by the polymerization indexes of their two blocks. The block copolymer consisting of a PS block with a degree of polymerization 390 and and a PVP block with degree of polymerization 150 will be designated as 390/150. Deformation experiments were carried out on thin films of blends of the two homopolymers with and without block copolymer additions. The nominal composition of the blend was 0.80 weight fraction PS homopolymer and 0.20 weight fraction PVP homopolymer. The PS homopolymer had a weight average molecular weight $M_w$ = 207 000 and a polydispersity index $M_w/M_n$ = 1.05 and was purchased from Pressure Chemical Co. The PVP homopolymer had $M_w$ = 240 000 and $M_w/M_n$ = 1.05 and was purchased from Polysciences Inc. Films about 0.5 μm thick were spun cast from benzene solutions onto rock salt substrates. After drying the films were annealed at 170 °C for 24 h under vacuum in order to approach equilibrium. The glass films could then be floated from the rock salt substrate onto the surface of a water bath and picked up on a ductile copper grid, whose grid bars had been previously coated with a thin film of PS. A brief exposure of the grid and film to the vapor of the solvent served both to remove the slack in the film (by relieving the biaxial orientation

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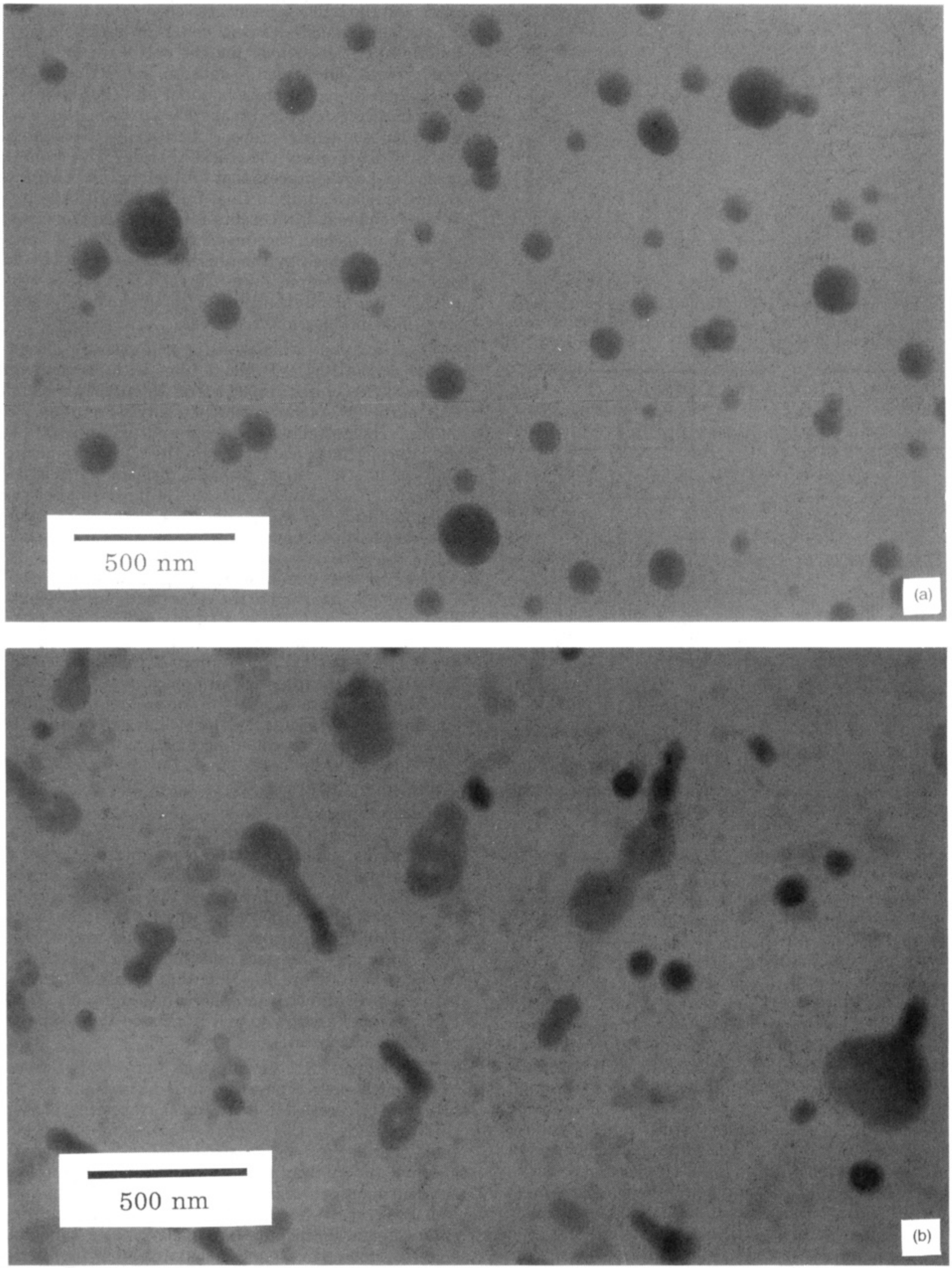

**Figure 1.** Transmission electron micrograph showing the microstructure of a thin film of a blend of 80% PS with (a) 20% PVP and no addition of block copolymer and with (b) 16% PVP and 4% 570–570 bcp where PVP particles appear dark from iodine staining. Both samples are imaged as-cast, i.e., without any annealing treatment.

induced by the casting procedure) and to bond the film to the copper grid. The grid was deformed in tension at a slow strain rate of $4 \times 10^{-6}$ s$^{-1}$ to a strain of about 0.05. The individual film squares of the grid were then inspected with an optical microscope, and a typical square was selected for examination by transmission electron microscopy (TEM). This grid square was cut from the grid by severing the surrounding grid bars with a razor blade. The PVP phase could be distinguished by exposing the film, after deformation, to iodine vapor, which forms ionic complexes with the PVP.[7,8]

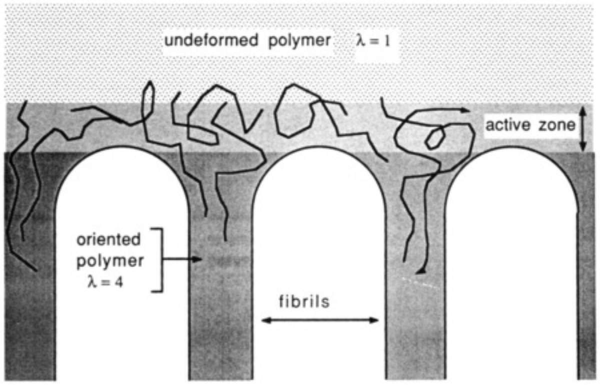

**Figure 2.** Schematic diagram of fibril drawing showing undeformed material ($\lambda = 1$) being drawn from an "active zone" into the crazed material ($\lambda = 4$).

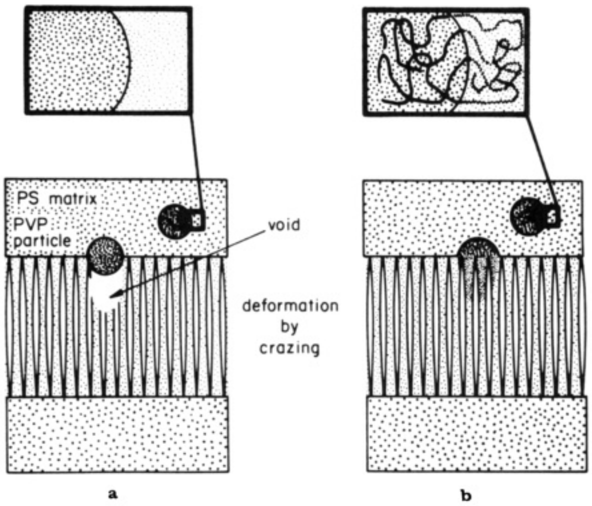

**Figure 3.** Schematic diagram of craze growth in a blend containing spherical second-phase particles when the stress transfer at the interface is (a) poor and voids are formed where the interface fails and (b) good and the second phase particle is effectively drawn into the crazed material.

## Results

**Particle Morphology.** The morphology of the as-cast film blend without block copolymer additions is shown in Figure 1a. The microstructure consists of small nearly spherical particles of PVP embedded in a matrix of PS. These particles range in diameter from about 30 to nearly 250 nm with the majority at about 100 nm. Figure 1b shows the change in morphology resulting from the addition of 0.04 volume fraction of a 570/570 block copolymer. There are now many nonspherical PVP particles, which demonstrates qualitatively the reduction in PS/PVP interfacial energy caused by the diblock copolymer addition. Subsequent thermal annealing above the glass transition temperature while the films were on the rock salt substrate caused the PVP phase particles to become spherical but did not however cause any large change in the particle size distribution. Due to very slow kinetics of the melt, the particle size distribution in the blend seemed more affected by the conditions of solvent casting than by the presence or absence of block copolymer.

**Crazing and Craze Breakdown.** Since both phases plastically deform by crazing, we review briefly what is known about the mechanisms of craze growth and breakdown. In pure PS for example, crazes are known to grow in width by drawing more polymer into the craze fibrils at essentially constant extension ratio $\lambda$ from a thin (<30 nm) fluidlike active zone at the boundary between the craze and the bulk, as illustrated schematically in Figure 2. Although such drawing could in principle go on indefinitely, thus converting the entire film into craze matter, such wide crazes do not form in practice. Rather, somewhere along the craze boundary (at the active zone) the craze fibril structure breaks down to form a large void, which subsequently grows subcritically to become a crack.[9,10] It is one of the cracks that develops from this craze breakdown process that ultimately will become the critical crack leading to final fracture of the specimen. While such breakdown occurs at so-called "intrinsic weak spots" in ultraclean specimens, the breakdown process is greatly accelerated by the presence of adventitious dust particles in the sample.[11] Fibril breakdown caused by these particles is probably the cause of fracture in most practical situations in polymers that craze.

This background is useful for understanding the behavior of the PS/PVP blend films without copolymer additions. As crazes in such a film widen, they encounter PVP particles. As shown schematically in Figure 3a, when one such craze attempts to draw the particle into its fibrils, the interface fails, leaving a void the size of the particle. Only small stresses can be applied to the particle itself before interface failure occurs, and so it remains spherical and undeformed. Figure 4a shows an electron micrograph of a craze in such a blend showing the voids and particles. When the particle is large, the subsequent void leads to fracture of the surrounding craze fibrils, and a large elliptical hole attached to the craze boundary develops. If the particle is small, the small void produced is not much larger than the craze fibrils, and the craze interface simply bypasses the particle, continuing to draw craze fibrillar material from the interface once the undeformed particle has been incorporated into the craze. Figure 4b shows a magnified view of a large PVP particle at the craze interface and a number of surrounding small, undeformed PVP particles within the craze.

If the PS/PVP interface is strong, however, this picture changes dramatically. Now as shown schematically in Figure 3b, the PVP particle is drawn directly into the craze fibrillar material at the craze interface, as if the particle interface did not exist. This process is shown in Figure 5a at low magnification at the craze interface in a PS/PVP blend that was doped with 0.04 volume fraction of 570/570 diblock copolymer. A higher magnification view of the craze interface and the drawn PVP particles can be seen in Figure 5b. Note that even small particles in this case are drawn from spheres into ellipsoids. Larger PVP particles are drawn and fibrillated to become part of several craze fibrils.

Whether the PS/PVP interface is strong (in the sense that enough stress can be transferred across the interface to deform the particle and prevent the formation of a large void) depends on the length of the blocks of the block copolymer itself. In our experiments the polymerization index of the PS was kept well above that required for entanglement, whereas the PVP block length was varied from well above to well below that corresponding to entanglement in the pure PVP melt. Figure 6 shows the behavior of the two extremes. Figure 6a shows the interface of a craze containing 0.04 volume fraction of a 570/570 diblock copolymer, and Figure 6b shows the interface of a craze containing the same volume fraction of 391/68 diblock copolymer. While the block copolymer with the long PVP block appears to produce a strong PVP particle interface, the diblock copolymer with the short PVP block produces a very weak interface. The deformation of the PVP particles can hardly be distinguished from the case

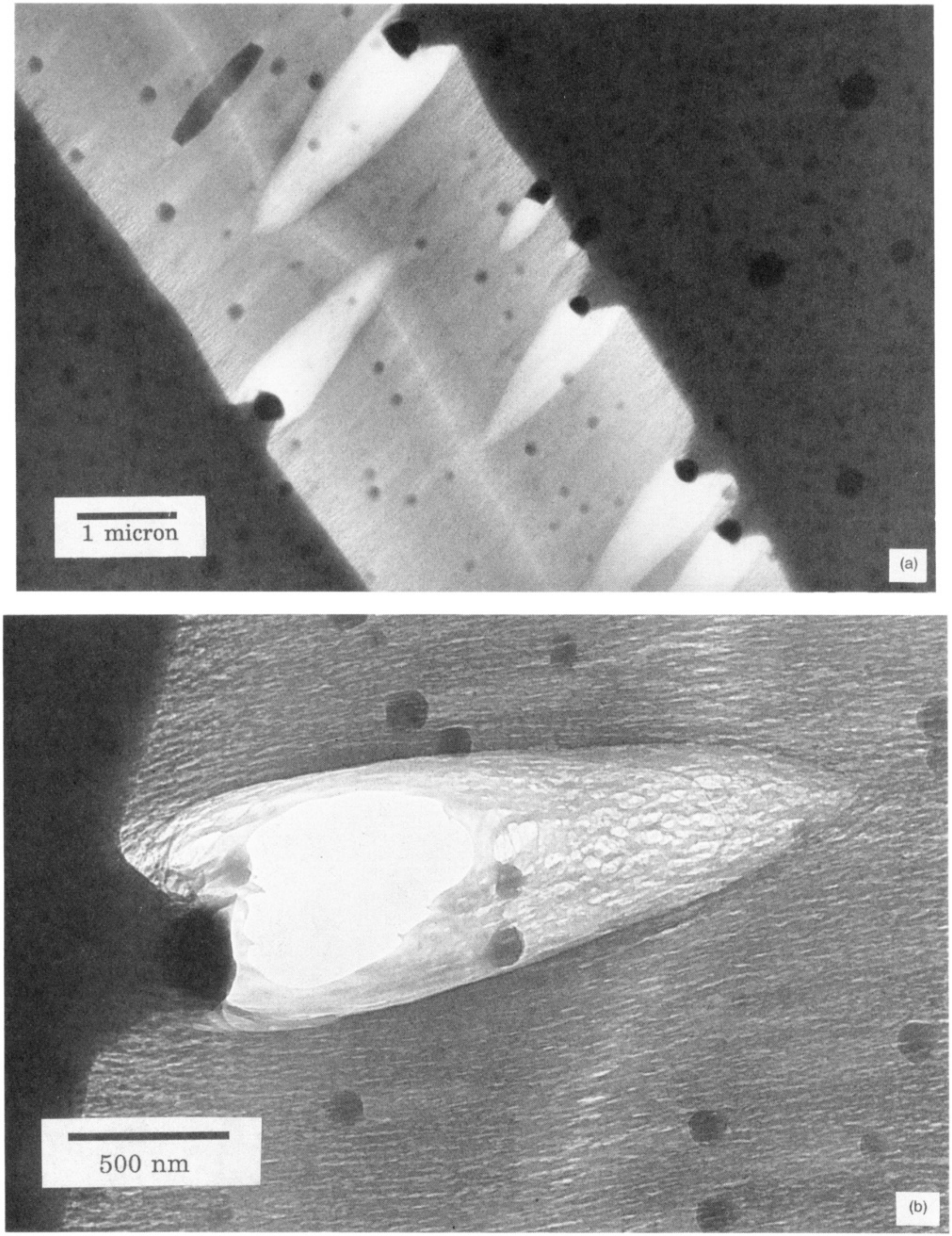

**Figure 4.** Transmission electron micrographs of a crazed film of a blend of 80% PS, 20% PVP and no addition of block copolymer. Note the voids in the crazed material created by the failure of the PVP particle interfaces.

where there is no block copolymer added. Large voids are formed at the large PVP particles and act as the "seeds" for subsequent craze fracture.

**Quantitative Analysis of Large Void Formation.** From the point of view of preventing premature fracture of the blend, the large voids shown in Figures 4 and 6b are

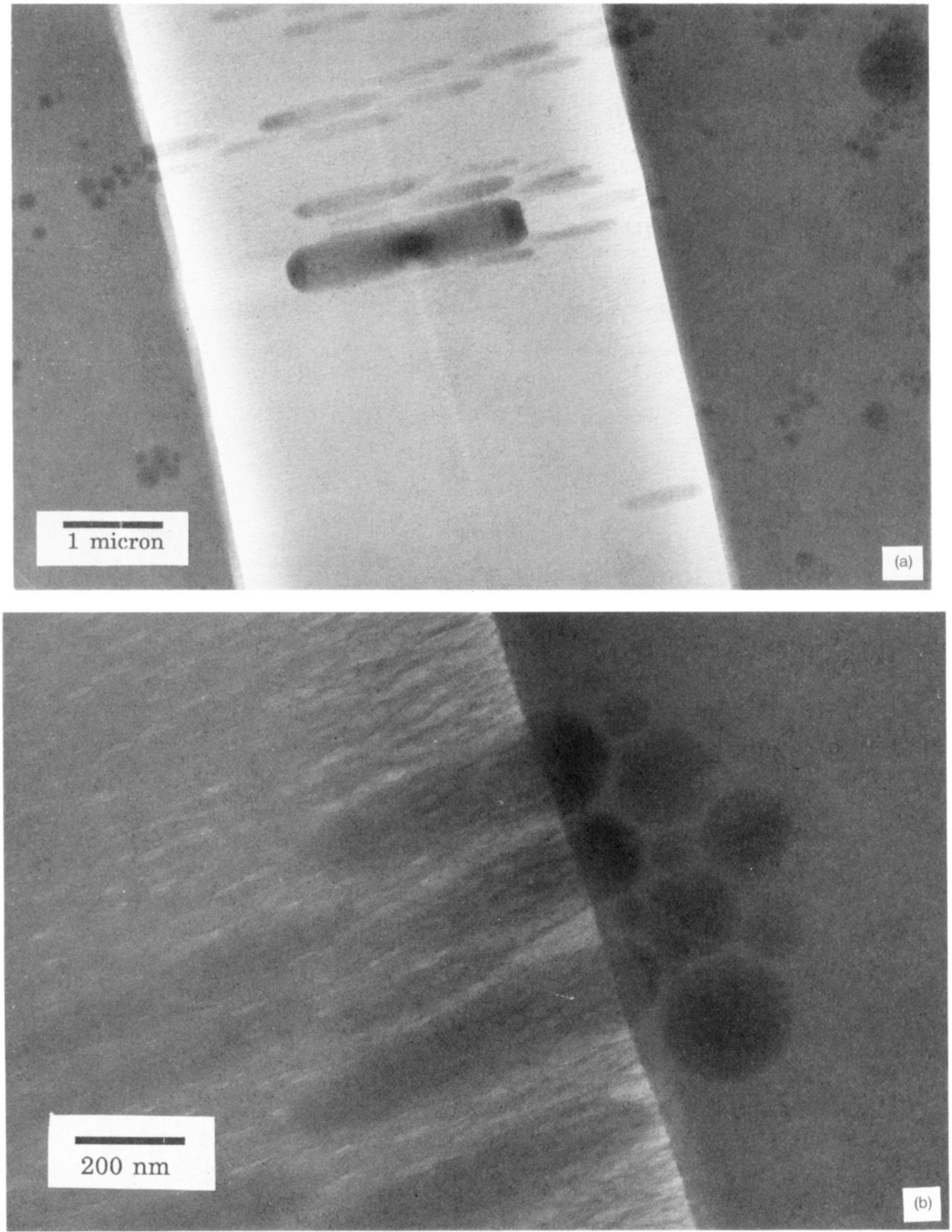

**Figure 5.** Transmission electron micrographs of a crazed film of a blend of 80% PS–16% PVP–4% 570–570 bcp. Note the deformed second-phase particles in the crazed area indicating a good stress transfer at the interface.

the most dangerous aspect of the weak PS/PVP interface. Accordingly we concentrate our attention on these voids in this section. The qualitative results of the previous section make it clear that the large voids are predominantly associated with the large PVP particles and therein lies a problem. If we simply count the large voids within crazes, relatively small shifts in the size distribution of PVP particles in our films can give misleading results. We have

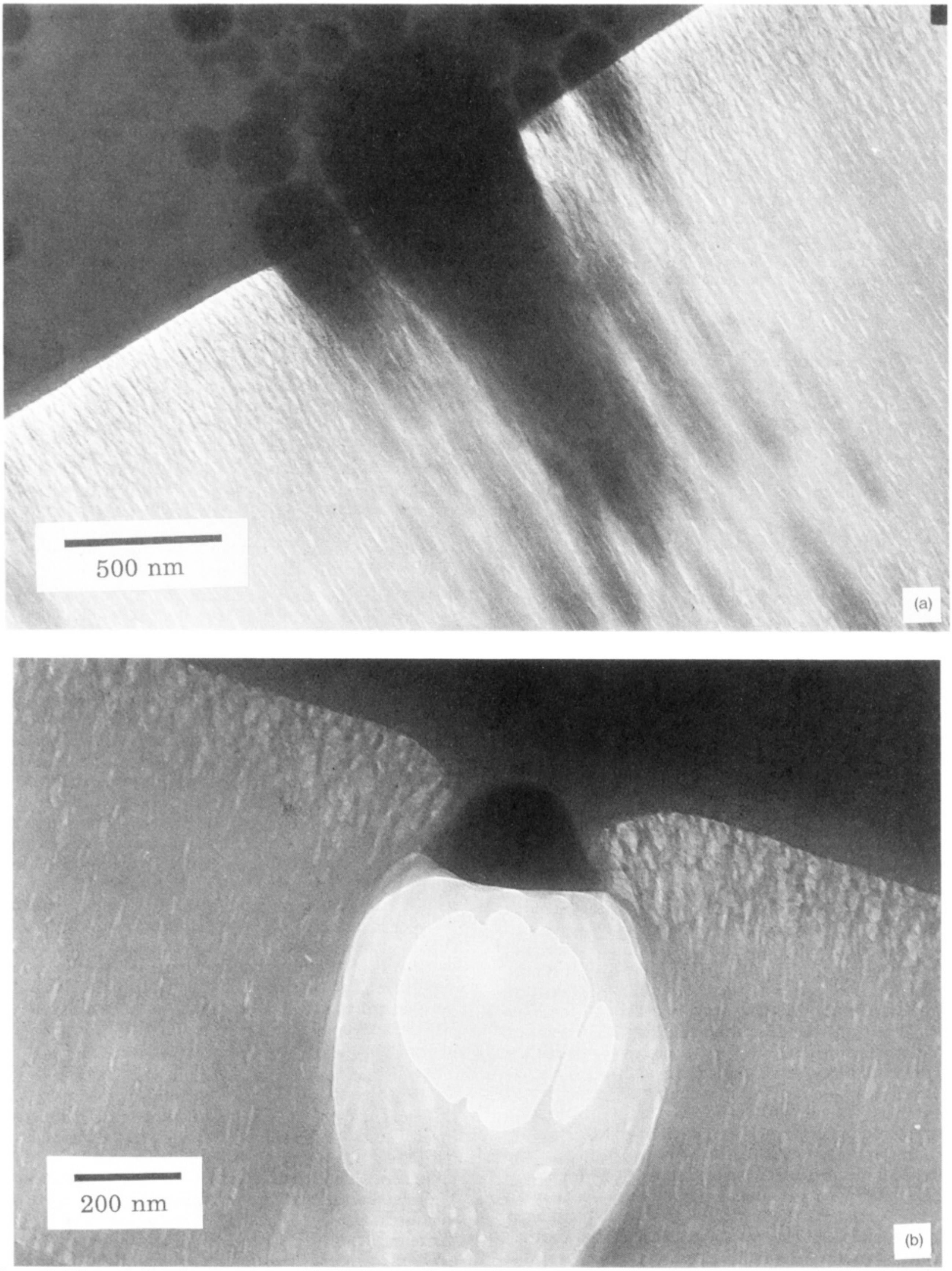

**Figure 6.** Transmission electron micrographs of a crazed film of a blend of 80% PS–16% PVP and (a) 4% 570–570 bcp and (b) 4% 391–68 bcp. Note how the short PVP block in Figure 5b is ineffective in promoting good adhesion of the particle interfaces.

therefore adopted the following procedure: We classify the particles observed within the crazes into a number of different size ranges based on their diameter. An example of the size range histogram for a typical film blend is shown in Figure 7. The craze surrounding each particle is examined to determine whether it gave rise to a large void by debonding of its interface. The fraction of such particles within each size range is the debonded fraction $f$. The

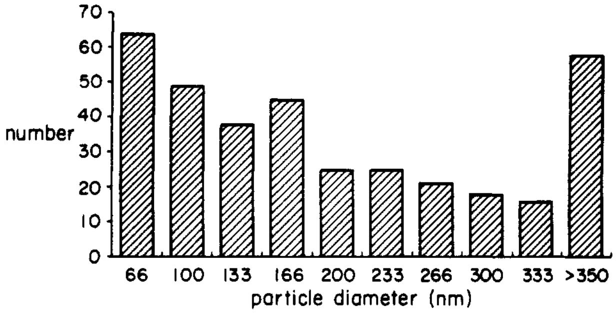

**Figure 7.** Typical size distribution of PVP particles in a PS–PVP blend with 4% 570–570 block copolymer. N.B.: The particle size distribution was relatively unaffected by the presence of block copolymer.

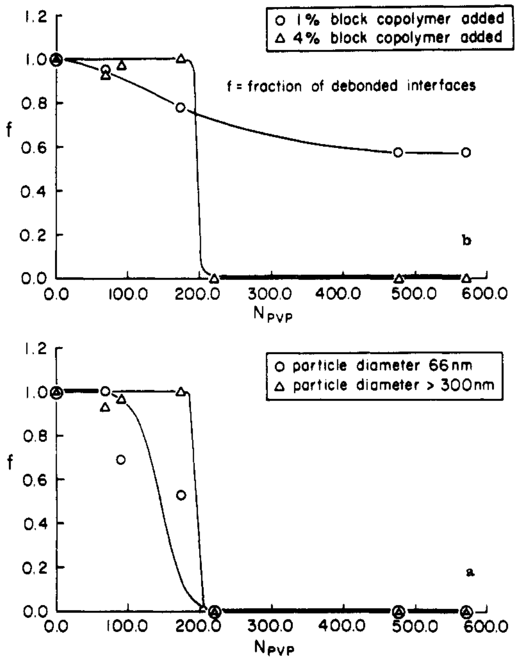

**Figure 8.** Fraction *f* of particles showing interface failure as a function of the degree of polymerization of the PVP block: (a) for two different particle sizes and 4% bcp added; (b) for the >300-nm particle size and 1% and 4% bcp added.

fraction *f* is then plotted versus the polymerization index $N_{PVP}$ of the PVP block in Figure 8a for two size classes of particles, those with diameters exceeding 300 nm and those between 50 and 75 nm (labeled 66 nm). It can be seen that for the larger particles there is a sharp transition in debonded fraction from 0 for $N_{PVP} > 200$ to 1 for $N_{PVP} < 200$. The transition for the smaller particle size is less abrupt and occurs at a lower $N_{PVP}$, but nevertheless the effect of PVP block length is strong even here. This size effect can be accounted for by a simple argument based on an energy balance between the elastic deformation energy stored in the particle and its immediate surroundings and the energy required to form the surfaces of the debonded interface. As shown by Gent and co-workers[12,13] in their experiments on debonding of glass beads in an elastomeric matrix, the critical stress for debonding is proportional to the inverse square root of the particle diameter; therefore, debonding becomes more favorable when the particle size increases, which is consistent with our experimental results.

The block molecular weight at which this transition takes place is remarkably close to what we expect the entanglement molecular weight $M_e$ to be for PVP. From a measurement of the craze fibrils extension ratio ($\lambda_{PVP} \sim \lambda_{PS} = 4$), we expect $M_e$ for PVP to be approximately the same as polystyrene, or 18 000, which converts to $N_{ePVP} = 173$.[9] Given the strong evidence that the important molecular weight for craze breakdown in homopolymers is $M_c \sim 2\ M_e$,[9] the critical molecular weight that marks the transition from unentangled melt behavior ($\eta \sim M$) to entangled melt behavior ($\eta \sim M^{3.4}$) of the zero shear rate melt viscosity $\eta$, the transition occurring for the asymmetric block copolymer at $M_e$ might appear strange at first. However, if we postulate that the onset of entangled behavior in the melt corresponds to an average of two entanglements per chain, consistent with $M_c \sim 2M_e$, the transition value observed for the block copolymer seems more reasonable. What is necessary for the transfer of stress across the PS/PVP interface is one "entanglement" between the PS block and the homopolymer PS chains on the PS side of the interface and one "entanglement" between the PVP block and the homopolymer PVP chains on the PVP side of the interface. The block on the PS side is long enough for all the diblock copolymer to have already satisfied this simple criterion, whereas the block on the PVP side varies, depending on the polymerization index of that block, from having more than one "entanglement" $N_{PVP} > N_{ePVP}$ to having less than one entanglement, $N_{PVP} < N_{ePVP}$. When $N_{PVP}$ falls below $N_{ePVP}$, there is on the average less than one entanglement per PVP block, and it is difficult to transfer the relatively high stresses needed to continue the craze widening across the PS/PVP interface without the interface failing.

All these results are for a relatively high concentration (volume fraction 0.04) of PS/PVP block copolymer in the blend. When the volume fraction of block copolymer is decreased to 0.01, the results of varying $N_{PVP}$ are less clear-cut as shown in Figure 8b. As before PVP blocks with polymerization indexes much less than $N_{ePVP}$ are ineffective in preventing debonding. However, at $N_{PVP}$ larger than $N_{ePVP}$ about 60% of the interfaces of PVP particles debond for particles larger than 300 nm in diameter. Clearly the amount of block copolymer at the interface, as well as the block length of the shorter block (the PVP block in this case) is important for preventing interface failure. Such a result of course could have been predicted from the previous experiments of Brown[14] on PS/PMMA block copolymers. He showed that for very long block lengths, the fracture toughness of a planar interface between PS and PMMA homopolymers on which the block copolymer was spread increased strongly with the areal density of block copolymer chains. He also showed experimentally that such chains fracture near the joint between the blocks.[15] Clearly if the areal density of PS/PVP block copolymer chains at our PS/PVP interfaces becomes too small, these chains will also fracture.

Herein lies the major problem with these thin-film experiments. Although excellent for allowing us to view the morphology of the blend and the craze microstructures leading to failure, there is no way to measure the local areal density of block copolymers at the PS/PVP interfaces. That these interfaces might not be at equilibrium is certainly an important question which we tried to address also by "annealing" films by exposing them to benzene vapor for 24 h. While the results of these experiments were qualitatively similar to those achieved after thermal annealing, the particle morphology is quite different and we are uncertain whether the quantitative differences observed between the two sets of samples were due to the difference in particle morphologies, difference in the amount of block copolymer at the interfaces, or both. In a separate study we observed (using forward recoil spectrometry) that most of the PS/PVP block copolymer with larger $N_{PVP}$ will form micelles at very low block copolymer concentrations in PS.[6] Once micelles have formed, the diffusion of block copolymer chains to segregate at the interface becomes painfully slow.

## Conclusion

Block copolymers of PS–PVP added to phase-separated blends of PS and PVP are effective in preventing interface failure provided that each block has a polymerization index of 200 or above. This critical polymerization index corresponds to the average chain length between entanglements of the homopolymers, clearly demonstrating the importance for the block copolymer to entangle effectively with both homopolymers to act as a mechanical reinforcer. If the polymerization index of either block is too small, the bcp will still act as a surfactant decreasing the interfacial tension and therefore modifying the microstructure but will not however prevent failure at the interface when high tensile stress is applied to it. The possibility to monitor separately the effect of the block copolymer on the particle morphology and on the interface mechanical strength is the main advantage of our new experimental technique using TEM. This method should be generally applicable to a wide range of polymer blend systems.

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**Registry No.** (PS)(PVP) (block copolymer), 108614-86-4; (PS) (homopolymer), 9003-53-6; PVP (homopolymer), 25014-15-7.