Notes to the Editor

Selective electron beam etching of multicomponent polymer systems

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A current area of interest in polymer science is the study of multicomponent polymer systems. These include blends, graft and block copolymers which exhibit various amounts of compatibility, depending on temperature and composition. Electron microscopy has become a central tool in elucidating the morphology of such systems. The major limitation to microstructural studies is obtaining sufficient contrast between the various phases. Usually one attempts to provide such contrast by the use of a selective stain such as osmium tetroxide. Unfortunately, most polymer systems of interest have intrinsic low contrast and specific chemical stains are difficult to find. We report here on the radiation induced contrast behaviour of the styrene–acrylonitrile (SAN)/poly(methyl methacrylate) (PMMA) system. Such a contrast mechanism will be operative in any multicomponent system when one of the phases responds in a significantly different manner to electron irradiation than the other.

Phase transition phenomena, especially spinodal decomposition and phase coarsening of the system styrene (72%)–acrylonitrile (28%) copolymer and poly(methyl methacrylate) were studied by McMaster[1]. Films (0.25 mil thick) of the blend containing 25 wt % SAN which corresponds to the critical point composition, or 75% SAN, far from the critical point were prepared by heating to a temperature of 180° or 265°C, sufficiently into the unstable region for spinodal decomposition to occur. The films were kept at these temperatures for various lengths of time to allow coarsening and then quenched below their glass transition temperature (105°C) in order to freeze in the structure of the separated and coarsened phases.

The heat treated films were then microtomed, and the thin specimens were examined in a transmission electron microscope (RCA EMU3B).

When first examined, no contrast between the separated phases was apparent. However, contrast developed after a few seconds under the electron beam†[1]. This phenomenon was not understood but was thought to be the result of the increase in scattering cross-section (mass thickness contrast) of the SAN-rich phase, presumably due to selective reaction of the regions of that phase with the diffusion pump oil vapours present in the microscope column.

A 25% SAN sample from McMaster's original work (thermally heated at 180°C for 30 min) was microtomed, and thin specimens mounted on 200 mesh copper grids for use in our investigation, to understand the origin of the above mentioned contrast mechanism.

McMaster's results of developing contrast with electron dose were reproduced using an RCA EMU3G microscope (*Figure 1*). The dark areas are the SAN-rich regions and the bright areas are the PMMA-rich regions. Since contrast as it appears on the micrograph is very much dependent on the microscope illumination conditions and the exposure time and on the printing process of the negative, there was need for an electron micrograph which would include both highly irradiated and minimally irradiated areas which would thus show the *true* change in contrast between the two areas. (It is well known that the human eye can be easily misled to erroneous evaluation of 'brightness' or 'darkness' depending on the relative location of 'bright' and 'dark' areas, see ref 3.) Such a micrograph cannot be easily produced in the conventional *TEM* because the electron beam has a

large diameter with a Gaussian distribution of the electron flux in this mode. However, the scanning–transmission mode of the scanning transmission electron microscope (*STEM* JEOL– 100CX) has a very narrow beam (less than 15 Å in diameter) as well can be made to scan a small rectangular area on the polymer specimen. After multiple scanning to produce a local high dose in the rectangular area the area scanned can be increased and a micrograph recorded of the combined multiply and singly scanned regions. To avoid rupture of the film due to local heating or charging by the high current density beam, it was necessary to choose the irradiated area to be near a grid bar which served as an electron and heat sink. Using the *STEM* mode, contrast between the phases was developed, the scanned area was increased and a micrograph taken (*Figure 2*). In the inner rectangle it is obvious that the bright areas are lighter than the area of background (outside the inner rectangle) and that the dark areas are
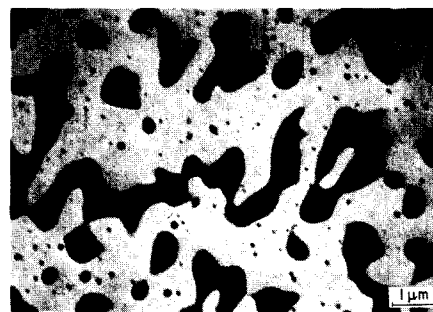

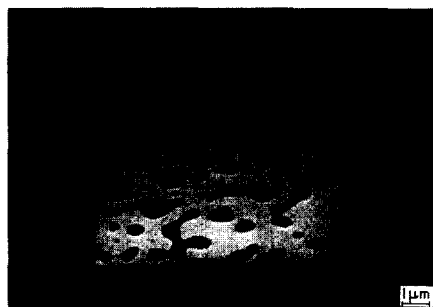*Figure 1* Micrograph of fully developed contrast from 25% SAN–75% PMMA blend. *TEM* bright field

Figure 2 *STEM* bright field micrograph of high dose irradiated area (small rectangle) and minimal dose irradiated area (surroundings) showing development of contrast due to thinning of PMMA-rich regions

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† The system polystyrene–poly(vinyl methyl ether) also behaves similarly[2].

as dark as the background. Thus the contrast is due to loss of material from the PMMA-rich (light) regions whereas the SAN-rich (dark) regions seem to have suffered no loss of material. The developed contrast is indeed mass thickness contrast, contrast due to different total mass of adjacent material which the electrons have to penetrate. What McMaster observed was not the darkening (thickening from diffusion pump oil deposition) of the SAN-rich areas, but indeed lightening (thinning, mass loss) of the PMMA-rich areas. Only adjustment of the exposure parameters in the microscope so as to please the easily deceived human eye made it appear the other way around!

For further proof of a preferential thinning of the PMMA-rich regions a heavily irradiated area was examined in the *TEM* mode (*Figure 3*). The picture is underfocused to enhance contrast. The middle part background is brighter due to the earlier extensive irradiation in the *STEM* mode. Three tones of grey are seen in the micrograph, the result of overlapping of two films one on top of the other. The lightest areas correspond to two etched (PMMA-rich) areas, the darkest areas to two unetched (SAN-rich)
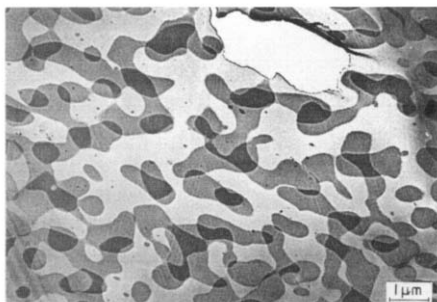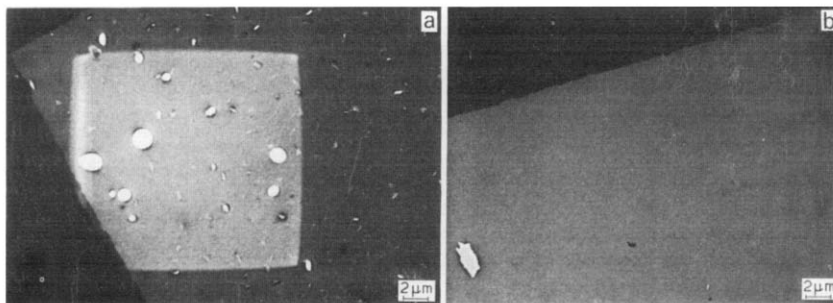

Figure 5 (a) *STEM* bright field micrograph of solution cast PMMA film showing thinning of high dose irradiated area (small rectangle). (b) *STEM* bright field micrograph of solution cast SAN film showing almost no effect on the high dose irradiated area

overlapping areas.

The selective etching mechanism is most vividly demonstrated in secondary electron imaging (*SEI* mode) of the irradiated film. The film was first exposed to the electron beam in the *TEM* mode to develop the contrast and then coated with a 100 Å layer of Pd—Au. It was then examined in the *SEI* mode at a tilt angle of 45° between the electron beam and the specimen plane. The micrograph (*Figure 4*) clearly shows the topography of the etched surface. On the higher (un-etched, SAN-rich) parts one can even see the grooves left by the microtome knife; on the other hand, these marks have been etched away in the lower parts (PMMA-rich).

The reason for this differential etching lies in the different electron beam—polymer interaction for the SAN and PMMA polymers. In general, electron irradiation results in chain scission and crosslinking, loss of mass, and destruction of crystallinity[4]. All of the above effects depend on the specific chemical and physical structure of the polymer, the temperature of the irradiated region, the total electron dose and the electron beam energy.

Both polystyrene and polyacrylonitrile polymers are of the crosslinking types[5–9]; polystyrene is in fact one of the most radiation stable polymers. Although SAN copolymer has not been extensively investigated, it is presumably also of the crosslinking type. The mechanism of electron beam damage in PMMA, on the other hand, depends on the total dose[9,10]. Initially, at low doses, PMMA degrades due to chain scission. However, at higher doses the predominant damage mechanism becomes crosslinking. Thus one expects SAN regions to be stable throughout the irradiation whereas PMMA regions should initially degrade but eventually become stable. This

behaviour agrees quite well with the observed resistance of the SAN regions and the thinning but not complete loss of the PMMA regions.

While it is possible broadly to classify polymers into crosslinking types and scission types[10], the actual final state of the irradiated material is very much dependent on the irradiation conditions (see for example ref 9). Perhaps the most practical approach in an electron microscopy study of multicomponent systems is to conduct standard irradiation tests (conditions chosen which will later be used to obtain micrographs of the actual polymer system) on each of the separate components. *Figures 5a* and *5b* show such tests conducted on pure PMMA and on the pure SAN copolymer. As is evident in *Figure 5a*, the heavily irradiated region has brightened considerably, indicating a significant loss of mass from PMMA. *Figure 5b* shows that SAN under these irradiation conditions is much more resistant to mass loss.

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Figure 3 Underfocused *TEM* bright field micrograph of high irradiation dose overlapped films. Note Fresnel fringe at edge of the dark regions indicative of a change of thickness
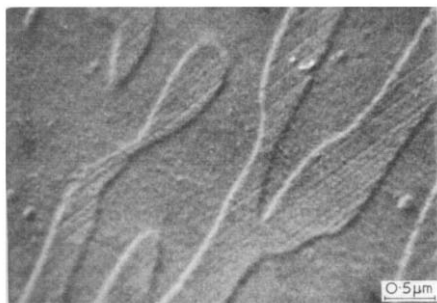

Figure 4 Secondary electron micrograph showing topology of a high dose region. Note grooves left by microtome knife in the thicker SAN-rich regions

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Thermodynamics of formation of high impact polystyrene

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The manufacture of high impact poly-styrene by the polymerization of an initially binary solution of polybuta-diene in styrene, has been extensively described in the literature in terms of general concepts of nucleation and phase inversion[1]. This note seeks to describe the process in terms of the nucleation of an equilibrium phase and spinodal decomposition occurring under isothermal conditions in a ternary system.

The dynamic system can be represented by a vector crossing the ternary polystyrene, polybutadiene, styrene phase diagram. This vector successively intersects the binodal curve which defines the miscibility gap and the spinodal curve which defines the limit of diffusional stability in the system. On a weight fraction basis this vector will be straight line.

The total Gibbs free energy of mixing of the components passes through a turning point with respect to composition at the binodal[2]. The coupled partial molal Gibbs free energies of mixing pass through a turning point with respect to composition at the spinodal. These two conditions coincide at the plait point which has the status of a multicomponent critical point[3].

A particular initial concentration, C_p, of polybutadiene will correspond to a vector which passes through the plait point. Initial concentrations of polybutadiene lower than C_p will give rise to vectors which intersect the mis-cibility gap on the polystyrene rich side of the plait point. This causes the polybutadiene rich phase at the opposite end of the tie line to nu-cleate[4]. Initial concentrations of poly-butadiene higher than C_p will convers-ely result in the nucleation of a dis-perse polystyrene rich phase.

The miscibility gap is a section of a surface in composition—temperature space. If the miscibility gap shrinks with increasing temperature the value of C_p will increase. This means that it will be possible for a single initial concentration to give rise to disperse polystyrene at a low temperature of polymerization and disperse polybu-tadiene at a higher temperature. Such an effect has been observed by Moore[5], and indicates that the miscibility gap slowly converges towards an upper consolute point. This shows that the system has a small positive value for both the enthalpy and entropy of mixing. This is in marked contrast to the behaviour of the polystyrene—poly(methyl methacrylate)—benzene system[6] which shows evidence of hav-ing fairly high negative values for the enthalpy and entropy of mixing. Poly-acrylate rubbers have never found favour as reinforcing agents for poly-styrene and this may be the reason.

As the polystyrene rich phase under-goes growth it rejects a shell of poly-butadiene. The initial solution process and the dissolution of initiator in-volves the formation of high molecu-lar weight polystyrene, which facili-tates the nucleation process.

The reaction proceeds, increasing the polystyrene concentration and bringing the composition of the meta-stable ternary mixture up to the spi-nodal. A corollary of the concentra-tion independence of the partial molal Gibbs free energy of mixing is that the surface excess Gibbs free energy with respect to liquid—liquid separation becomes zero. This results in the poly-mers present undergoing a severe ex-pansive conformational transition. This is the cause of the viscosity peak known as phase inversion[7].

Once within the spinodal the sys-tem encounters a condition where the coupled partial molal Gibbs free ener-gies of mixing assume an inverse de-pendence on concentration. The mix-ing volume shows a large excess value, causing anomalous dilatometric mea-surements of the reaction rate to be obtained[8]. The spinodal condition occurs in a miscibility gap tending to show an upper consolute point and the system rapidly undergoes spinodal decomposition[4]. This tends to give two continuous interdigitated networks. The necessity to continue stirring des-pite the viscosity increase may be due to the need to disrupt a continuous polybutadiene matrix.
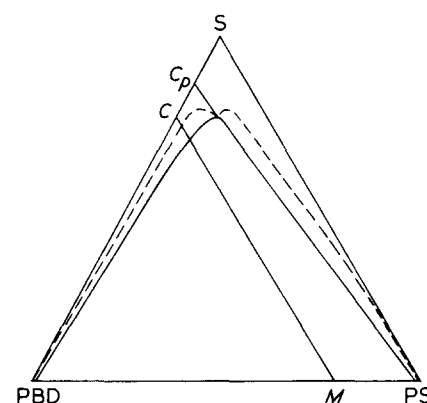

Figure 1   Schematic diagram of the styrene (S), polystyrene (PS), polybutadiene (PBD) system based on the data of Welygan and Burns (ref 2). C_p, the binary composition corresponding to an intersection of the reac-tion vector and the critical point. *CM*, a reaction vector corresponding to the normal manufacturing process

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