polymer papers

Morphology of ellipsoidal latex particles

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Ellipsoidal polystyrene latex particles, a few micrometres in length and very suitable for use as models for colloid studies, have been prepared and characterized. Polystyrene spheres were embedded in poly(vinyl alcohol) (PVA) and the resulting film stretched at 200°C to two film draw ratios, 1.4 and 2.35. The deformed particles were examined by light scattering and some were extracted for transmission electron microscopy. The light scattering results, analysed using Rayleigh–Gans theory, were in very good agreement with the electron microscopy. The ellipsoids were biaxial (within the limits of experimental error). Those deformed to the highest draw ratio deviate slightly from true ellipsoids, having rather sharper ends. The PVA deforms by a process of necking, which is non-uniform on a large scale, so that over the whole film there can be a considerable variation in draw ratio. However, particles recovered from any small, local area of the PVA film show a size distribution almost as uniform as that of the starting material. The effective draw ratio of the particles is found to be considerably greater than that of the matrix.

(Keywords: ellipsoid; latex; polystyrene; light scattering; transmission electron microscopy)

BACKGROUND AND PREVIOUS WORK

The use of well characterized spherical polystyrene (PS) latex particles as model colloids in the studies of various surface and colloid phenomena is well documented[1,2]. However, there are relatively few reports of work on model colloids of non-spherical particles, especially well characterized ones[3]. This is because non-spherical particles such as ellipsoids are more difficult to prepare and to characterize. Recently, a method of preparing ellipsoidal polystyrene latex particles with predesigned axial ratio was reported by Nagy and Keller[3]. The starting material was spherical PS latex particles. These were obtained commercially and thus were not fully characterized with respect to the various surface properties. The spherical PS particles were embedded in a film matrix of poly(vinyl alcohol) (PVA) and stretched above the T_g of the PS to various film draw ratios. Recovery of the deformed particles was achieved by dissolution of the matrix with solvent followed by centrifugation.

STARTING MATERIALS AND FABRICATION OF PRODUCTS

Polystyrene latices containing well characterized monodisperse spherical latex particles were prepared by various polymerization procedures[4]. The matrix material, PVA, prepared by an improved technique from poly(vinyl acetate) by alkaline hydrolysis, gave homogeneous films free of contaminating products and devoid of lumps. Details of the purification and characterization of these two starting materials are given elsewhere[4,5].

Film containing spherical PS particles was prepared by mixing together calculated weights of the appropriate latex and the PVA solution and casting the mixture on Perspex plates placed on a levelled platform. Film strips $3\times 9\,\mathrm{cm}^2$ were cut and the film thickness measured by a micrometer. The strips were first preshrunk, in order to remove any residual strain from casting, by dipping them briefly (no more than 5 s) in an oil-bath maintained at $200\pm 3°$C. They were then clamped one at a time in a metal frame and stretched to pre-set length, corresponding to various film draw ratios, in the oil-bath at $200\pm 3°$C. Total immersion time in the oil-bath was about 10 s. The two ends of the strips (about 1.5 cm each) and the edges were discarded and only the centre portion of the strip was retained and used in the recovery of the deformed particles.

However, it became obvious later that the stretching was not uniform; the deformation of the film is visible by the formation and propagation of a neck, so that some parts of the film stretched more than others. Thus the embedded PS is deformed to different extents in different parts of the strip. This contributes to a higher degree of polydispersity in size of the recovered ellipsoidal particles. To improve the size uniformity of the recovered elongated particles, strips of the PVA film with embedded spherical PS particles were marked and divided into grids with an ink marker before stretching. After stretching, only those grids whose lengths corresponded as closely as possible to the expected film draw ratio were cut and recovered. All other grids, as well as those at the ends and edges of the strips, were again rejected. The size distribution of particles recovered in this manner was compared with those prepared earlier when this precaution was not taken.

The ellipsoidal particles embedded in the stretched PVA matrix were recovered by dissolving away the PVA in a solvent, followed by a series of cleaning procedures[4] to give, finally, a stable dispersion of particles in water.

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In order to investigate the stretching process, films were stretched in a PL 'Minimat' miniature tensile testing machine. The resulting stress–strain curve at 200°C is shown in *Figure 1*. The curves were essentially identical whether the PVA film contained latex particles or not. These curves are consistent with the formation and propagation of a neck in yielding material. The yield and necking were more pronounced at lower temperatures, but were still present to a significant degree at 200°C, the highest temperature we could use without obvious degradation of the PVA matrix.

TRANSMISSION ELECTRON MICROSCOPY

Three types of particle were investigated by TEM: the original UK3 spheres and samples that had been stretched in PVA to film draw ratios of 1.4 and 2.35, which will be referred to as UK314 and UK3235 respectively. Experimental details are given in the relevant sections.

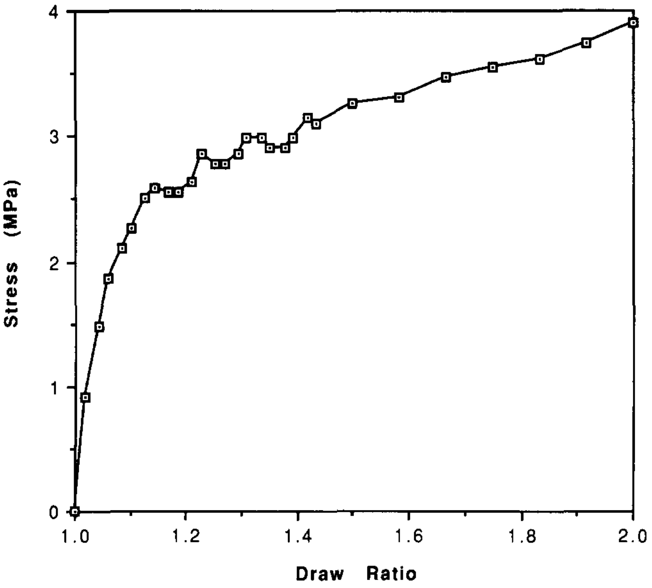

Figure 1 Stress–strain curve of deforming PVA matrix at 200°C

General appearance of particles

Stretched particles were recovered from the matrix in the manner described above. Particles were inclined to clump together, but could be separated, to some degree, by brief treatment in an ultrasonic bath while still suspended in water. Recovered particles were spread thinly on carbon-coated TEM grids for observation. Spheres were placed on the same grid as each of the ellipsoid preparations for direct calibration.

One particle of each type is shown in *Figure 2* with ellipses drawn for comparison. From the micrographs it was clear that:

(a) The outline of each particle is smooth. There are no obvious surface irregularities.

(b) Both the spheres and the stretched particles appear to be of fairly uniform size. A number of particles in each group were measured. The average measurements are shown in *Table 1* (columns 5 and 6), together with the standard deviations (see further details below).

(c) There are very few distorted particles to be found among the stretched particles.

(d) The ellipsoids of the higher stretched UK3235 group do not appear strictly elliptical in section, but seem to have rather pointed ends (compare *Figure 2c* with *2f*).

Investigation of the shape and size distributions

TEM was used to study the details of size and shape of the ellipsoids. Particles of each type, recovered from large areas of stretched film, were measured and the particle draw ratio assessed. The size distribution was found to be Gaussian. The particle draw ratio of these large samples of UK314 and UK3235 particles, together with the standard deviations, are shown in column 9 of *Table 1* (results taken from ref. 4). The particle draw ratio is simply calculated by raising the measured axial ratio to the power 2/3. In the micrographs of this large sample there is a considerable uncertainty (of the order of 15%) in the absolute magnification. However, the particle draw ratio determination and the statistics are unaffected by this.

Further particles were recovered from very much smaller areas of stretched PVA film. The magnification was carefully checked and spheres were always included

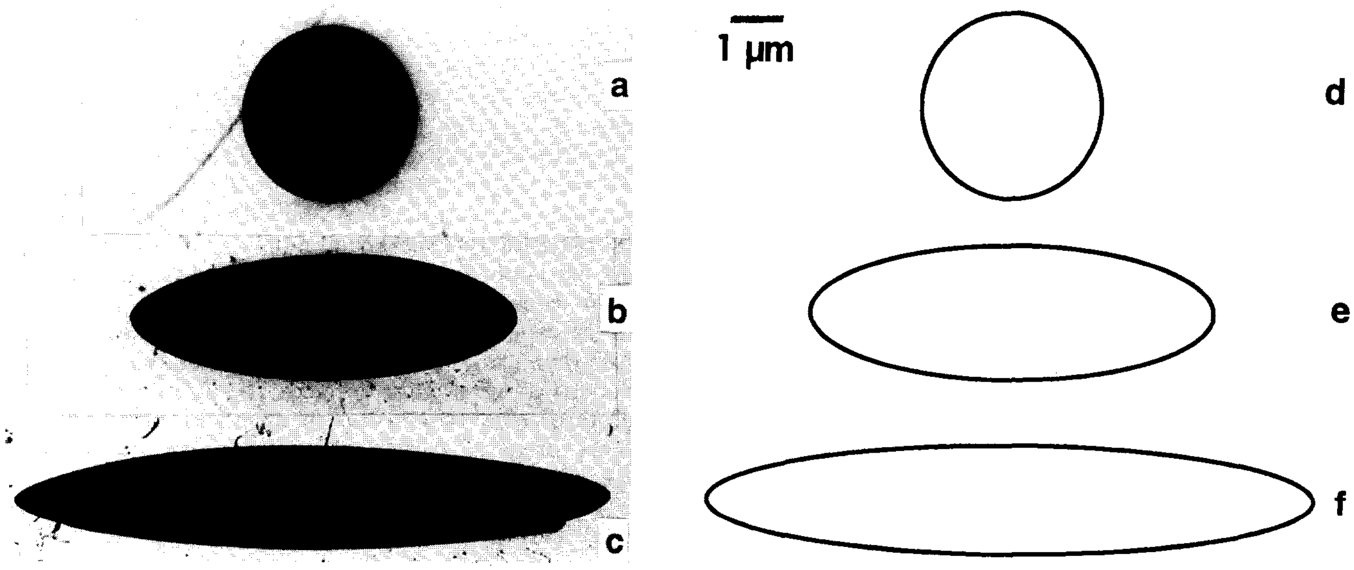

Figure 2 TEM of particles with film draw ratios (a) 1, (b) 1.4 and (c) 2.35 together with ellipsoids of the same axial ratios (d)–(f)

Table 1

Sample	Film draw ratio	Film birefringence	Number of ellipsoids	Size of particles		Draw ratio			
				Major axis (nm)[a]	Minor axis (nm)[a]	Film	*E/m*[a]	*E/m* large sample[a]	Light scatt.
UK3	1	0	30	3727 (4)	3727 (4)	1	1 (4)	1 (4)	1
UK314	1.4	0.011	22	7831 (3)	2841 (5)	1.4	1.9 (4)	1.9 (7)	1.8
UK3235	2.35	0.025	34	12300 (3)	2189 (6)	2.35	3.2 (5)	3.2 (6)	3.3

[a] Numbers in parentheses show standard deviations (%)

as a calibrant, to enable absolute determination of size of these particles. First the particles were measured, as before, and the average particle draw ratio assessed. The average values of the major and minor axes, together with the particle draw ratio and standard deviations, are shown in columns 5, 6 and 8 of *Table 1*. Note that, although the number of particles measured is much lower, the standard deviation is smaller than for the previous sample. We believe this to be a consequence of the fact that the film draw ratio is well defined locally, although it varies appreciably over the whole film.

Having established the size and effective draw ratio of the particles we were interested to see if they were truly biaxial or, to some degree, triaxial, i.e. not circular in section when cut normal to the long axis. Three experimental methods were adopted to investigate this. None was wholly satisfactory, but each gave an experimental limit to the possible ellipticity of cross-section; in each case the conclusion was that the section is only slightly (if at all) different from circular.

Sectioning. Three sample types were sectioned using an LKB ultramicrotome: PVA alone, PVA with spheres embedded and PVA with UK3235 ellipsoids embedded.

The pure PVA cut well. Because PVA is soluble in water, sections were floated onto dimethyl sulfide; when picked up they appeared very little wrinkled or distorted.

Much more difficulty was experienced when cutting PVA with embedded polystyrene. This was due to the mismatch in the moduli of the two materials. PVA is much softer than PS, so that the general effect was akin to cutting butter with rice embedded in it. Spheres embedded in PVA were not well anchored and were dragged through the matrix, tearing holes. The final PS sections always appeared elliptical and were in most cases wrinkled, the wrinkles being at right angles to the knife direction. Thicker sections appeared less distorted than thin ones. Often a section was found at one side of a hole in the PVA, more often, but not always, on the side at which the cut had ended. In some case the PS sections were displaced from the holes and lay on the matrix. Some of these features can be seen in *Figure 3*. Absolute measurements are not useful here, since a range of diameters can be obtained by cutting through spheres. However, sections of spheres should all be circles; in fact, they were not circles, and the axial ratio of the PS sections was found to be 1:1.22 (with a s.d. of 0.07 over 20 measurements). The short axis of undetached PS sections was always parallel to the cutting direction, which (together with the observed direction of the wrinkles) indicates that the apparent ellipticity was a cutting artefact.

When ellipsoids (rather than spheres) were embedded, the PS was anchored more effectively, especially when the cutting direction was perpendicular to the major axis. Holes were pulled in the PVA in some, but not all, cases. Some PS sections were wrinkled, but many seemed undistorted. Sections were cut at a number of angles within three degrees of the long axis of the ellipsoids; little difference in axial ratio was found between cutting directions. Within experimental uncertainty one third of the sections measured were circular. The overall average axial ratio of all samples was 1.09 (s.d. 0.07). As for the cut spheres, the shorter axis was always parallel to the cutting direction. From this experimental evidence it seems very probable that the true cross-section was circular, with any ellipticity caused by deformation during cutting. In the worst case the axial ratio is given as 1.09 by this method.

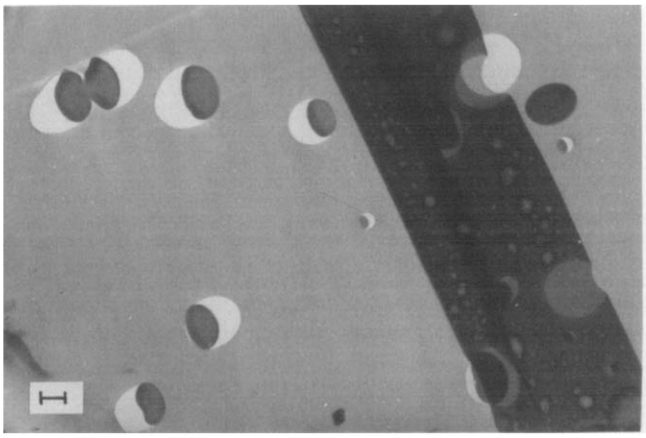

Figure 3 Transmission electron micrograph of a section including embedded spheres. The knife mark (upper left) indicates the direction of cutting. There is also a fold (dark region), which is normal to the cutting direction. Many of the sectioned spheres are wrinkled normal to the cutting direction owing to the action of the knife. Note that the sphere upper right appears distorted in the opposite direction, but this is due to its detachment from the film and subsequent rotation. Scale bar represents 1 μm

Shadowing. Spheres and UK3235 ellipsoids were deposited, together, on carbon-coated grids and shadowed at an angle of approximately 30°. Spheres were used for calibration. Compared with the shadow from a sphere of given diameter, the shadow length will be longer for an ellipsoid resting with its major axis at right angles to the substrate and shorter if the major axis is parallel to the substrate. Only ellipsoids oriented at right angles to the shadow direction are useful to estimate any possible triaxiality. The shadow length was measured for 13 spheres and nine UK3235 particles. From the (rather few) results we have, it appears that the shadows of the UK3235 particles are slightly shorter than would be expected from ellipsoids of circular cross-section, indicating that the particles may be triaxial, lying with the larger

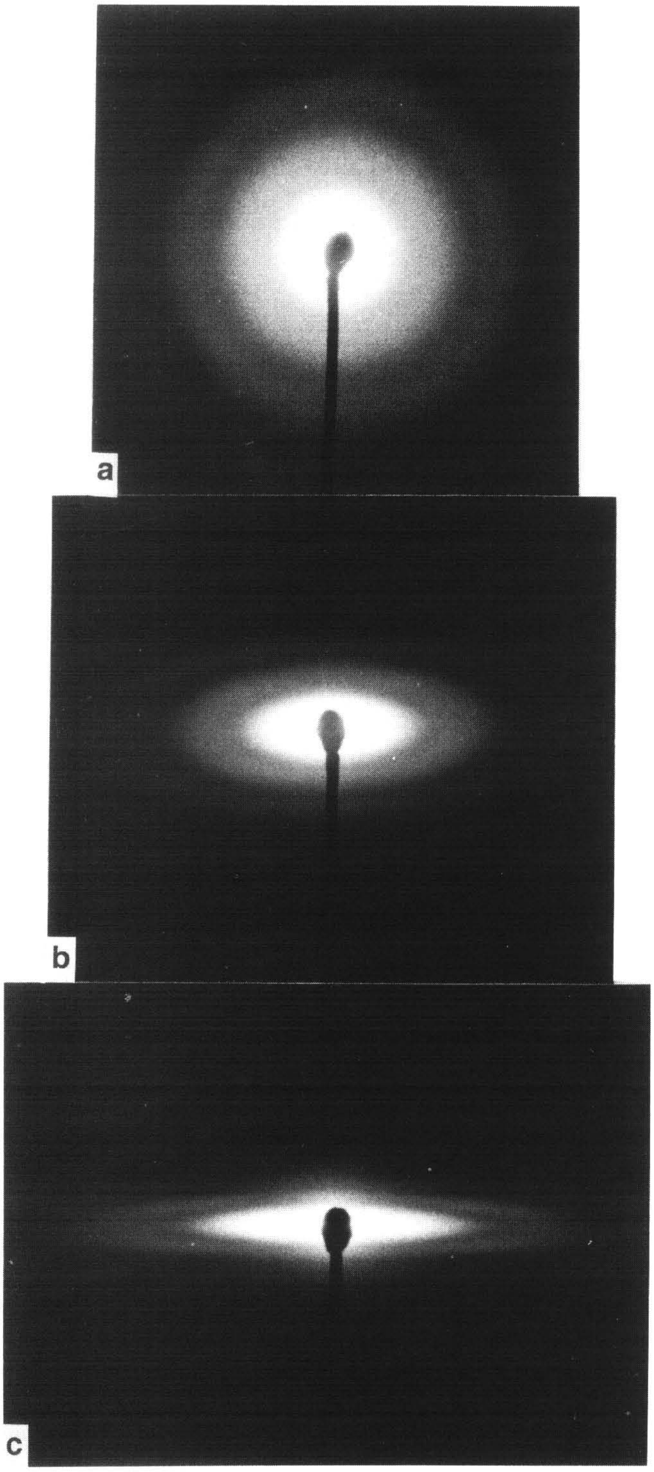

Figure 4 Light scattering patterns from films with draw ratio (a) 1, (b) 1.4 and (c) 2.35

of the two minor axes parallel to the substrate. A value for the axial ratio of 1.1 (±0.1) is indicated; clearly the uncertainties are such that a circular cross-section is just within the experimental errors.

Volume calculation. From the measurements of the particles (listed in *Table 1*) the volumes can be calculated. We would expect that the volumes of the stretched particles would be the same as those of the spheres. Working from the average measured dimensions and assuming the deformed particles to be perfect ellipsoids of revolution, we calculate volumes as 1.09 (s.d. 6%) for UK3235 and 1.03 (s.d. 7%) for UK314; these are relative volumes, taking the volumes of an average sphere as 1. Note that these figures are independent of any error in the magnification calibration of the TEM since spheres and ellipsoids were on the same grid. The volumes of the ellipsoids work out to be rather higher than the average volume of the original spheres, although the numbers are just within the experimental errors. However, we know that the UK3235 particles are not perfect ellipsoids of revolution, but that the ends are more pointed. This would lead to a slight overestimate in the particle volume, which is difficult to quantify. Once again, the results indicate that the particles may be biaxial within the limits of the experiment.

None of our methods for assessment of biaxiality is without experimental difficulties and uncertainties; in all cases it would be advisable to perform more measurements. However, all three techniques indicate that the particles are either biaxial or, at worst, triaxial with an axial ratio of minor axes of 1:1.1, with the uncertainty on the latter figure being ±0.1.

LIGHT SCATTERING STUDIES

In order to characterize the deforming latex spheres, we have utilized laser light scattering. This is, of course, much less laborious than particle recovery and TEM, and also has allowed us to follow, dynamically, the deformation process as the PVA film is drawn.

In initial studies wide-angle scattering from UK3 particles in the PVA film was performed using a 5 mW He–Ne laser. The scattered light was recorded on a special red-sensitive photographic plate or else videotaped. The films used contained only 0.004–0.007% spheres. This avoids overlap of spheres so that the scatter is characteristic of the dilute system.

The scattering patterns recorded for film draw ratios of 1, 1.4 and 2.35 are shown in *Figure 4*.

Qualitatively, the appearance of the scattering of the undeformed particles (*Figure 4a*) is essentially the Fourier transform of the refractive-index difference between the particles and the matrix; it shows a beautiful Bessel-function-modulated pattern with four orders visible.

As shown in *Figures 4b* and *4c* the scattering from the stretched particles becomes anisotropic. Now multi-order scattering with pseudo-elliptic peaks is observed. This is, of course, in line with our qualitative expectations.

In order to obtain a quantitative assessment of particle ellipticity from the light scattered image, we must consider, theoretically, the scattering of light from isolated ellipsoids with a refractive index different from the surrounding medium.

Normally the assessment of scatter from particles as big as UK3 (3727 nm) would be extremely difficult, since the size is large compared to the wavelength of light (651 nm). It would involve the use of Mie theory[6], probably without a closed analytical result, or else extremely computation-intensive numerical procedures.

The classical Rayleigh–Gans (RG)[7] theory is restricted to particles with a size less than $\lambda/(\eta-1)$ where η is the refractive index of the particles. However, when the particles are in a matrix of high refractive index (η'), the size limitation becomes $\lambda/(\eta-\eta')$. In the present circumstance, the latex spheres have a refractive index of 1.59, which is only slightly greater than that of the PVA matrix

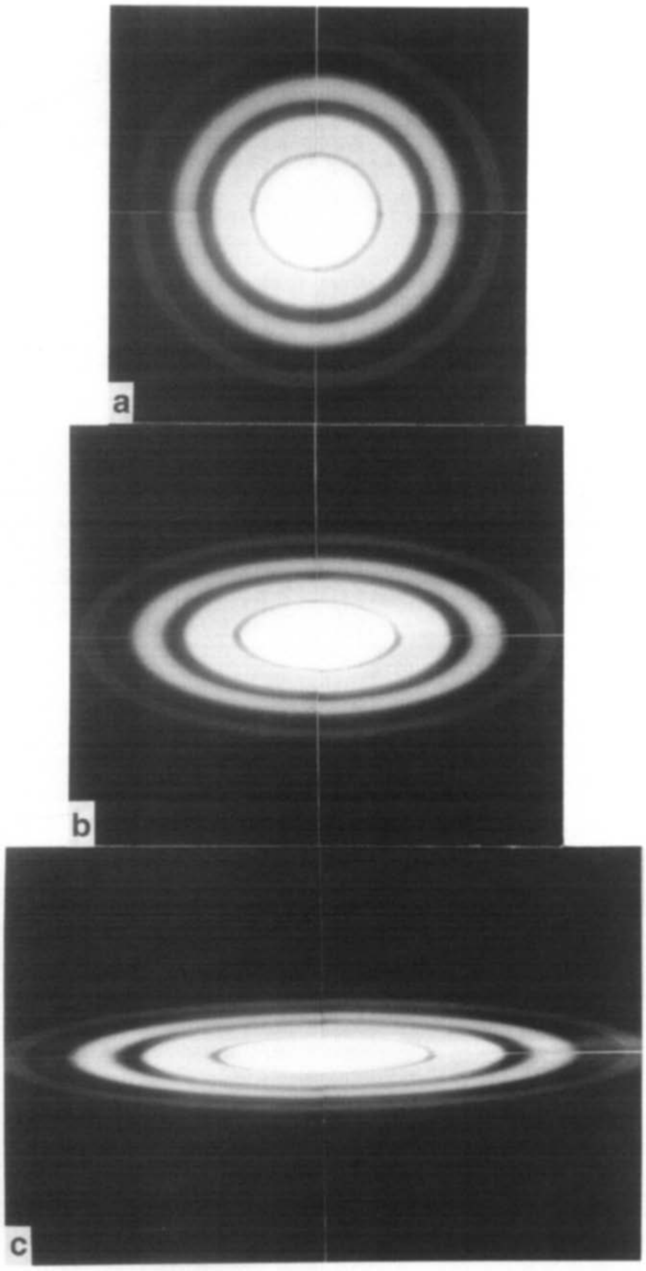

Figure 5 Simulated scattering by Rayleigh–Gans theory for particles of draw ratio (a) 1, (b) 1.8 and (c) 3.3

at 1.52[5,8], so that the size limitation is $\simeq 14\lambda$. So, at least to a first-order approximation, we can treat the scatter as RG. The basis of the theory is that the 'applied' field to which each volume element is exposed differs in neither phase nor amplitude appreciably from the original wave, and that the (weak) scattered wave leaves the particle without further modification. The calculation for ellipsoids is relatively straightforward.

Figure 5 shows computer-calculated intensities corresponding to particle draw ratios of 1, 1.8 and 3.3 from RG theory. It is clear from the close agreement with the actual light scattering patterns from undeformed particles that, indeed, use of the RG theory is justified, even for particles as large as UK3 (compare *Figure 4a* with *Figure 5a*).

At a film draw ratio of 1.4, the best match for the observed scattering pattern is obtained with a particle draw ratio of 1.8. This, in fact, agrees well with the observed particle draw ratio from the TEM (1.9) but considerably *exceeds* the film draw ratio of the PVA matrix. Similarly, the film with draw ratio of 2.35 gave light scattering that corresponded to particles with a draw ratio of 3.3, again in good agreement with the TEM (3.2). It is clear that the particles suffer a deformation, which, though very uniform, is considerably greater than that of the deforming PVA film in which they are embedded. The origin of this effect may lie in the induced anisotropy of the PVA film.

We conclude that laser light scattering (coupled with RG theory) can give reliable estimates of the aspect ratio of even large deforming latex spheres in a PVA matrix.

The uniaxial stretching process is the equivalent of a biaxial compression of the embedded latex particles. This results in a pressure within the softened polystyrene. If the PVA matrix was mechanically anisotropic, this could lead to stress concentrations at the smallest radius of curvature of the ellipsoid, which could split the PVA matrix, resulting in greater extension of the ellipsoid than the matrix.

In order to assess this effect, we have measured the induced birefringence in the PVA film during drawing. As can be seen in column 3 of *Table 1*, there is indeed considerable optical anisotropy, increasing with draw ratio, strongly suggesting mechanical anisotropy.

CONCLUSIONS

This technique is clearly capable of giving ellipsoidal latex particles, with dimensions almost as closely controlled as the starting latex spheres. They are biaxial, within experimental uncertainty. The PVA matrix, however, deforms by a process of necking and neck propagation; this makes the control of effective draw ratio difficult and leads to an increase in dispersion of particle size unless particles are recovered from selected areas only.

Rayleigh–Gans theory gives a good description of the light scattering properties of the embedded particles and agrees well with results from transmission electron microscopy. Both techniques suggest, however, that the effective draw ratio of the ellipsoids is considerably greater than that of the PVA matrix. This may be a result of induced mechanical anisotropy in the matrix. At the highest draw ratios the particles deviate somewhat from true ellipsoids, having sharper ends.

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