Ordering in Aqueous Cellulose Hydrolysate Dispersions: An Ultra-Small-Angle X-ray Scattering Study

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The ordering phenomena of various ionic species in solutions or dispersions, such as synthetic and biological polyelectrolytes and spherical colloidal particles, have been intensively studied.[1] In an effort to expand the study to rodlike polyion systems, we became interested in cellulose derivatives first and initiated a systematic study of cellulose hydrolysates by using an ultra-small-angle X-ray scattering (USAXS) technique. During the course of our study, our attention was drawn to papers by Marchessault and Gray et al.,[2,3] which reported that the dispersions were found to separate into anisotropic and isotropic phases above a critical concentration and the concentrations of the hydrolysates in these two phases did not much differ from each other. The second finding was highly unexpected to us, since similar phase separation is known to occur with a much greater concentration difference as clearly shown by the vapor−liquid condensation equilibrium for ionic polymer latex particle dispersions.[4] Thus we examined this problem by using the USAXS technique and report here briefly the relevant results.

Cotton linter (15 g) was treated with 65 wt % sulfuric acid (150 mL) at 70 °C for 30 min. The hydrolysate was washed with ion−exchanged water by successive dilution and centrifugation to remove excess acid. Further purification was carried out by dialysis against Milli-Q water (Millipore, Bedford, MA). The dispersion was concentrated to 5.9 wt % by ultrafiltration, dispersed by subsequent ultrasonic treatment, and kept as a stock dispersion. The stock dispersion was diluted with Milli-Q water for measurements at 1.0, 2.0, and 4.0 wt %. The size and shape of the hydrolysate particles were determined using a transmission electron microscope on the dilute dispersions. Though the micrographs are not shown here, the particles were rodlike (as seen from Figure 1 of ref 3), and the average length and width were 1500 and 100 Å, respectively. The analytical charge density was determined by a conductometric titration to be 0.8 μC/cm^2.

The USAXS apparatus was described in previous papers.[5,6] Single crystals of Ge were used in the Bonse-Hart camera system.

Desmeared scattering intensities from salt-free dispersions at various concentrations are given as a function of the magnitude of the scattering vector q $(=(4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle and λ the wavelength of an X-ray, 1.54 Å) in Figure 1. Clearly there exists a distinct single broad peak for all the concentrations except for 1.0 wt %, at which the peak became barely detectable. The peak position shifted toward smaller q and the intensity became lower with decreasing hydrolysate concentration.

As has often been pointed out (see, for example, ref 1), a single broad peak has been observed for various ionic polymer solutions and ionic colloidal particle dispersions by small-angle X-ray scattering and small-angle neutron scattering measurements.[1a] The "polyelectrolyte" peak is known to be sensitive toward added salt; The peak position for synthetic and biological polyelectrolytes shifted toward lower q and the peak disappeared at high salt concentrations. Thus, we thought it important to obtain the USAXS profiles for the present system at various salt concentrations. In Figure 2, the scattering intensity observed is given at four concentrations of added NaCl. The peak is seen to become smaller with increasing salt concentration and disappeared at [NaCl] = 10^{-2} M. As was the case for the polyelectrolytes, the salt addition caused disruption of the ordered arrangement.

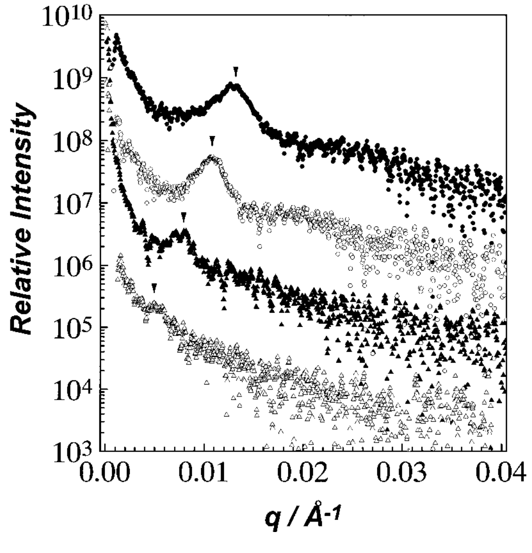

Figure 1. USAXS profiles of cellulose hydrolysate dispersion at four concentrations. From the top to the bottom, the concentrations of dispersions are 5.9 wt % (●), 4.0 wt % (○), 2.0 wt % (▲), and 1.0 wt % (△). The curves were shifted vertically by a factor of 20.

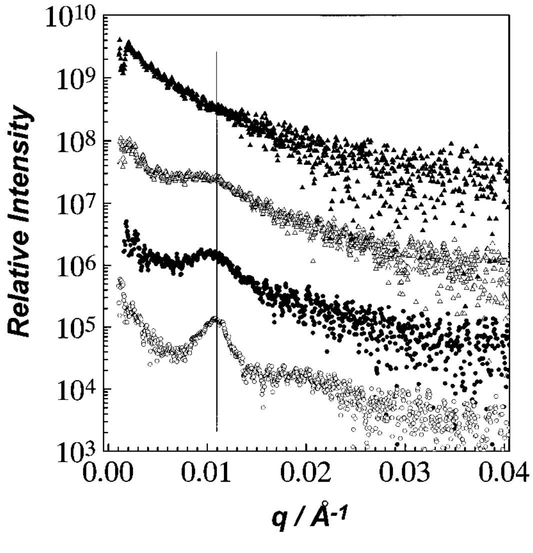

Figure 2. The influence of NaCl added on the USAXS profiles of cellulose hydrolysate dispersions. The concentration of cellulose hydrolysate is 4.0 wt %. From the bottom to the top, the concentrations of added salt as NaCl are 0 M (salt-free) (○), 10^{-4} M (●), 10^{-3} M (△), and 10^{-2} M (▲). The curves were shifted by a factor of 20.

The difference between the present and polyelectrolyte cases is that the peak position in Figure 2 did not change with salt concentration, whereas the "polyelectrolyte" peak did change as mentioned above. In the case of latex particles and colloidal silica particles, the

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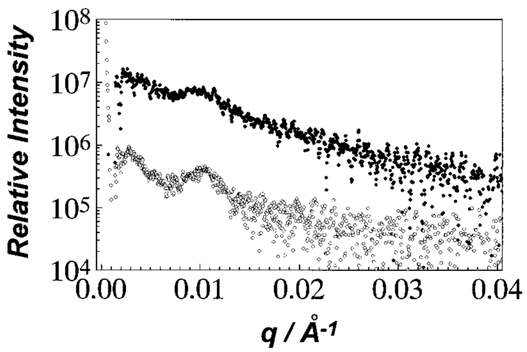

Figure 3. USAXS profiles observed from the upper isotropic (top curve, black circle) and lower anisotropic (bottom curve, open circle) phases. The concentration of cellulose hydrolysate is 4.0 wt %. The profiles were shifted vertically by a factor of 20.

peak position in the small-angle X-ray scattering[7] and that of the interference function by dynamic light scattering[8] shifted toward higher q with increasing salt concentration. The microscopic observation of latex dispersions[9] showed that the interparticle spacing in crystalline regions decreased with increasing salt concentration, which is in accord with the shift of the peak position in refs 7 and 8, if one accepts that the observed single peak reflects paracrystalline-distorted ordered arrangement of the solute ions in solution or dispersions and the peak position corresponds to the interparticle spacing. It seems that the size change of solute ions or particles due to salt addition is an important factor in determining the direction of the shift of the peak position. The observed shift for the hydrolysates is an intermediate case between the flexible polyelectrolytes and the rather rigid latex or silica particles, and might reflect the intermediate flexibility. Further quantitative study is necessary.

The dispersions at 4.0 and 5.9 wt % showed phase separation into two phases with a clear boundary, as was reported previously.[2,3] The hydrolysate concentration in the lower, anisotropic phase and that in the upper, isotropic phase did not much differ, confirming measurements by Gray et al. which showed that they differed from each other only by about 20%, though at much higher initial concentrations. We performed the USAXS measurements for the two phases by covering either of the two phases with a lead plate. The results are shown in Figure 3, demonstrating no practical difference between the two phases.

It is amazing that such polydisperse rodlike ionic particles showed similar scattering profiles as synthetic and biological polyelectrolytes and colloidal particles. Also surprising is that the almost identical scattering profiles were found for the anisotropic and isotropic phases. Our inference at present is that there are a number of randomly oriented "localized ordered domains of rodlike particles" in the isotropic dispersions and these ordered domains form much larger structures to cause optical anisotropy in the lower phase. However, to be consistent with the observations that the concentrations in the isotropic and anisotropic phases are about the same, the structures of high particle density in the anisotropic phase have to coexist with regions of low density (voids for an extreme case as found for polymer latex dispersions[10]).[11]

References and Notes

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(11) By taking into account fingerprint textures (onion coat structures) of a spacing of 20 μm photographed by previous authors (refs 2 and 3) and by us, we tentatively speculate about the domains and their distribution as follows: the particles show chiral nematic arrangement around an axis with an interparticle spacing corresponding to the USAXS peak (1300, 800, 580, and 480 Å for 1.0, 2.0, 4.0, and 5.9 wt %), the size of which is about 1500 Å × 1500 Å × 20 μm. The domains are distributed at random in the isotropic phase whereas they form large "brick house" structures in the anisotropic phase. Of course, this is a highly simplified picture and, in reality, the domain size would be polydisperse and the "brick house" structure is not space-filling, but many of them are jointly oriented to give rise to the "fingerprint" structures found by microscopy.

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