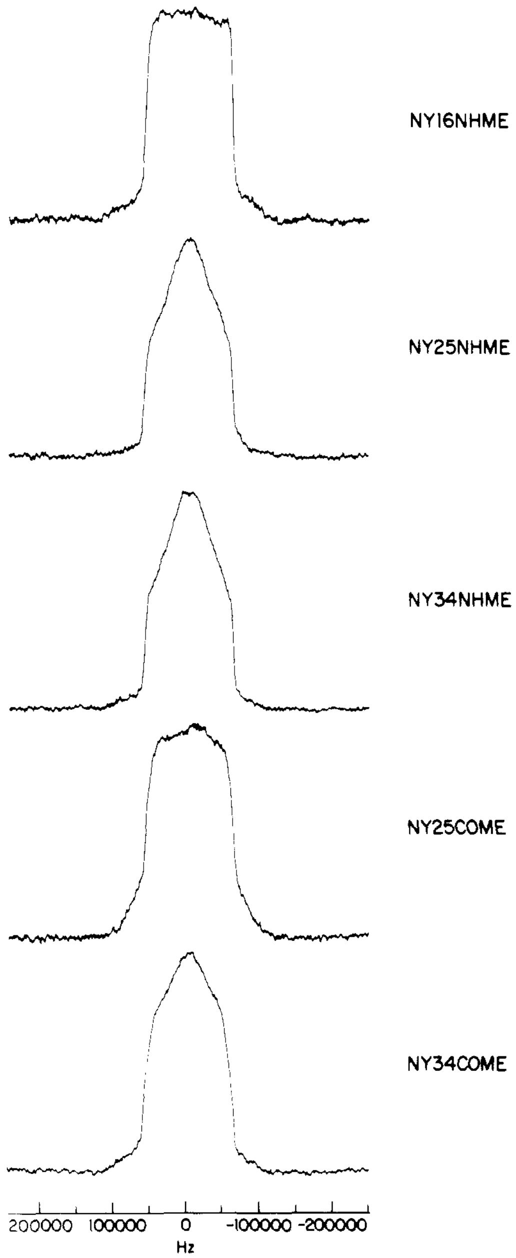

Figure 2. Fully relaxed ^{2}H NMR spectra at 97 °C of nylon 66 polymers that have been selectively deuteriated in the diamine moiety at the C_1 and C_6 carbons (NY16NHME), the C_2 and C_5 carbons (NY25NHME), and the C_3 and C_4 carbons (NY34NHME) and in the adipoyl moiety at the C_2 and C_5 carbons (NY25COME) and the C_3 and C_4 carbons (NY34COME).

Figure 2 illustrates fully relaxed ^{2}H NMR spectra at 97 °C for each of the nylon 66 polymers that have been selectively deuteriated on the five chemically distinct methylene carbons. These spectra illustrate that the type of motion extant at each methylene site is not the same. A qualitative interpretation of these line shapes indicates that the motion at both pairs of methylene carbons α to the amide linkage are motionally inhibited relative to the interior methylene groups. A full analysis of the dynamics of each methylene group including the temperature dependence and the heterogeneity of the rates and amplitudes of librational and internal rotation modes is in progress. Preliminary results for each of the methylene groups in the crystalline domains indicate that there is considerable internal rotational freedom as well as librational motion well below the melting point and the motion of all five methylene groups is quite similar at all temperatures above the Brill transition. Methylene groups in the noncrystalline domains exhibit substantial internal rotational motion as well as libration substantially below the glass transition temperature and the motion of both pairs of methylene groups α to the amide linkage is inhibited relative to that of the interior methylenes. These data should allow a critical examination of various models[9,10] of macromolecular dynamics at the segmental level.

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Registry No. Nylon 66, 32131-17-2.

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Static Light Scattering Studies of Suspensions of Charged Rodlike Tobacco Mosaic Virus

Static light scattering (SLS) in the visible region is a suitable technique to study structural properties of interacting polyelectrolyte systems. The accessible scattering vectors q range from 0.6×10^{-2} nm^{-1} to 3.3×10^{-2} nm^{-1} at a wavelength $\lambda = 488$ nm. A thoroughly studied model system for spherical polyelectrolytes are charged polystyrene spheres (latex) in aqueous solution.[1,2] In order to investigate the influence of structural anisotropy one can choose the model of stiff rods. The tobacco mosaic virus (TMV) particle with length $l = 300$ nm, diameter $d = 18$ nm, and surface charge of about 1000 e$^-$ is a good example of this type.[3] LS work has been reported concerning its dynamic properties in buffer solutions.[4] However, no attention has been paid to effects of interaction at very low ionic strength, which have been shown to become strong in the case of latex spheres. Almost nothing is known either experimentally or theoretically about the interaction potential between highly charged nonspherical finite sized Brownian particles and about the resulting structural correlations in such systems. Allowing for flexibility of the linear particles, a large number of systems have been investigated of which we would like to mention NaPSS since

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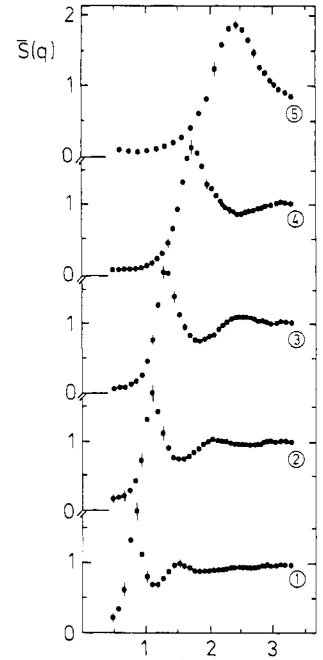

Figure 1. Static structure factors of solutions of TMV as function of scattering vector for five different concentrations: (1) $c = 0.11$ mg/mL; (2) $c = 0.27$ mg/mL; (3) $c = 0.43$ mg/mL; (4) $c = 1.05$ mg/mL; (5) $c = 2.07$ mg/mL.

this is the only linear system for which information on static and dynamic correlations is available from LS.[5]

In order to get more insight into the structural and dynamic properties of anisotropic polyelectrolytes we have undertaken LS work on aqueous suspensions of charged TMV at very low ionic strength. In this paper we report on the results of static light scattering.

Experimental Section. Aqueous solutions of TMV with a concentration of 11 mg/mL at pH 7 were obtained by courtesy of Professor C. Wetter (University of Saarbrücken). Five samples were carefully prepared between 0.11 and 2.07 mg/mL corresponding to $0.044c^* \leq c \leq 0.845c^*$ with the overlap concentration $c^* = 1$ virus/L^3 or 2.45 mg/mL. The actual concentration was determined by UV absorption at $\lambda = 260$ nm. Since we are interested in systems with strong Coulomb interactions, the ionic strength of the suspensions had to be minimized. The lowest ionic strength was accomplished by adding about 0.5 mL ion-exchange resin (MB-Serdolit, Serva Corp.) to each sample. It is known that this will damage the virus after some time, especially in the case of high concentration and small sample volume. The following steps ensure well-defined measuring conditions in the sample.

Between two successive measurements a run with a reference sample (toluene) in the total q region is carried out to correct for slow laser power fluctuations. In order to compare the quality of the final samples, static light scattering measurements are performed for all samples before adding ion-exchange resin. Also, electric conductivity and pH values are measured. After treating the samples with MB-Serdolit they are controlled the same way several times during the next hours. The lowest ionic strength is reached approximately when the H_3O^+ concentration of the solution determined by its pH value coincides with that derived from conductivity measurements. This was reached after about 10 h. The intensity curves remain stable afterward for a few days so that well-reproducible light scattering results are obtained. After some days the intensity compared to that of untreated samples begins to drop. This fact, together with UV absorption measurements, indicates a decreasing TMV concentration. Between the measurements the samples are stored in the refrigerator at 5 °C.

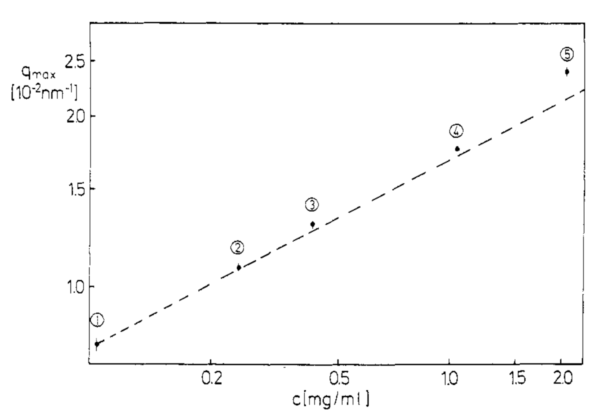

Figure 2. Double logarithm plot of $q_{\max}$ versus concentration. Numbers refer to concentrations given in Figure 1. The dashed line corresponds to $q_{\max} \propto c^{1/3}$.

The charge of the TMV particles, determined from pH and conductivity values to be a few hundred e^-, is considerably smaller than the surface charge. This is due to the well-known effect of counterion condensation, treated thoroughly by Manning for linear polyelectrolytes.[6] An instrument suited for static and dynamic light scattering investigations was used in the experiments (ALV, FRG). During the measurements the sample cell was stabilized at 25 ± 1 °C. Data have been taken at scattering angles between 16° and 150°. Below 16° some aggregation or dust particles perturbed the scattering intensity. At concentrations above 1 mg/mL samples turned out to be slightly opaque. In order to compare the intensity of different concentrations, the extinction coefficient measured at the laser wavelength $\lambda = 488$ nm was used to correct data accordingly. Multiple scattering within the probe volume can be neglected, as has been verified by depolarized light scattering.

Results and Discussion. The scattered intensity $I(q)$ has been measured as a function of scattering vector q for the five samples. The results were normalized by concentration c. Analogous to the LS theory for latex spheres, the static structure factor $S(q)$ for stiff rods in solution is given by the relation[7]

$$I(q) \propto NF(q)\bar{S}(q)$$

Here $F(q)$ is the one-particle form factor in the isotropic phase and N is the total number of macromolecules in the illuminated volume. In contrast to spherical particle systems $\bar{S}(q)$ depends on the form factor $F(q)$.[7] Subscripts refering to polarization of the incident and the scattered light have been omitted since our measurements refer to polarized scattering only. Our intensity data are divided by the measured form factor to give $\bar{S}(q)$ (Figure 1). A liquidlike structure is obtained which is particularly pronounced at lower concentrations. The second maximum can be followed up to $c \leq 0.4c^*$. As expected the $\bar{S}(q)$ curve approaches to 1 for large q. A distinct broadening of the curves occurs at higher concentrations. The scattering vectors of the peak maxima $q_{\max}$ as displayed in Figure 2 scale as $c^{1/3}$ at low c; at higher concentration a deviation is observed towards an exponent of $^1/_2$.

At concentrations $c < c^*$ the overall behavior of $\bar{S}(q)$ is very similar to that of charged latex spheres in solution at low ionic strength.[1] The very small values at low q resemble the small osmotic compressibility of the system. The structure developing with increasing q expresses the fact that a mean local order of the particles exists due to the electostatic interaction. It vanishes when enough salt is added. In the case of latex spheres the width of the main peak of $S(q)$ decreases and the peak height increases with increasing concentration, finally leading to the phase transition to liquid crystalline order. In contrast, the main peak for TMV broadens with increasing concentration below c^* and its height remains constant. Intuitively this can be understood in terms of the shape anisotropy of the rods. When the mean distance $\bar{r}$ of the rods becomes comparable to the rod length L, a given segment of a given rod interacts with all segments of the randomly oriented neighboring rods; that is, the "Bragg condition" is much less well defined than in the case $\bar{r} \gg L$.

Our results at the highest concentrations may be compared with data obtained for linear NaPSS in aqueous solutions at low ionic strength.[5] Since it is not possible to give a form factor for NaPSS because of its flexibility, the scattered intensities have to be compared. However, as the shapes of the $I(q)$ and $\bar{S}(q)$ curves for TMV differ only slightly the latter may be used for comparison. NaPSS samples close to $c = c^*$ produce a definite but broader peak without any further structure. Applying similar physical arguments as above, this difference may be attributed to the flexibility of NaPSS, thus supporting the interpretation of the maximum as also being due to spatial correlations.

Concerning theoretical work, only a small amount of information is available on the static properties of charged rodlike systems applicable to TMV in solution. Regarding $\bar{S}(q)$, an analytical expression has been derived for weakly interacting systems[7] ($c \ll c^*$). On the other hand, results of Monte Carlo simulations for suspensions of charged rodlike macromolecules have been reported using a model consisting of two or three segments along a rod.[8,9] Good qualitative agreement is found between our experimental results and those obtained by Monte Carlo simulations with regard to the broadening of the $\bar{S}(q)$ curves and the scaling of the peak maximum as function of concentration. As derived from the experimental results, the scattering wave vector of the latter deviates from the $c^{1/3}$ law near the overlap concentration, tending toward a larger exponent. It remains to be seen by quantitative analysis whether the experimental results can be fitted by the (relatively simple) dumbbell or the three-bead model,[8,9] thus allowing one to extract information on the interaction potential between charged rods.

In conclusion, we have presented clear evidence of local ordering in dilute suspensions of charged rodlike macromolecules in the light scattering regime. The static structure factor exhibits a pronounced peak even in the neighborhood of c^*, where the length of the particles becomes comparable to their mean distance. Since spatial correlations are known to affect considerably the dynamical properties of charged Brownian particles at low ionic strength,[1,2] our results will also help one to understand the dynamic light scattering spectra. These investigations will be discussed in a further paper.

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