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### Scattering studies of the associating behaviour of ionomeric and nonionomeric micelles in a selective solvent

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Scattering studies of the associating behaviour of ionomeric and nonionomeric micelles in a selective solvent

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A study has been made comparing the micellization behaviour of diblock copolymers polystyrene-*b*-poly(*tert*-butylstyrene) and sulphonated polystyrene-*b*-poly(*tert*-butylstyrene) in the polar, selective solvent, dimethylformamide. In this solvent, poly(*tert*-butylstyrene) is insoluble and forms the compact core surrounded by either the solvated unfunctionalized polystyrene or the sulphonated polystyrene. The aggregation behaviour in the dilute solution region was studied using static and dynamic light scattering. The results confirmed that the ion-containing polymers form micelles with much larger overall size despite their smaller aggregation number as compared to those of the nonionic polymer. This behaviour can be interpreted as arising from the repulsion effect of the ionic charges on the polymer sequences in the corona. Viscosity measurements are also performed to show the effect of the aggregate size on the rheological properties.

## INTRODUCTION

Many studies have demonstrated the interesting behaviour and the effect of selective solvents on diblock copolymers. In solvents that are selectively good for one of the polymer component blocks micellisation has been observed<sup>(1,2)</sup>. The formation of such a system is described by a closed association model, with an equilibrium existing between monomers and micelles with narrow size distributions. In general, the micellar structure consists of a compact core composed of the unsolvated blocks surrounded by a halo of the solvated blocks.

Ionomers are polymers containing small fractions of ionic groups on the backbone of hydrocarbon chains. When dissolved in polar solvents, such as dimethylformamide, these exhibit dramatic changes in rheological properties and molecular dimensions as compared with flexible long chain polymers in the dilute solution region. This has been explained as due to the solvent polarity. The explanation is based on the ionisation of the salt groups and resulting repulsion between the ionic groups along the polymer chains<sup>(3)</sup>. As a result of this property of the ionic groups, one would expect the rheological properties and number of associated chains per aggregate and dimension of diblock copolymer micelles might be dramatically changed by introducing a small fraction of ionic groups on one of the polymer block components. Micelles with ionic groups either in the internal core or in the halo can be prepared and studied depending on the selective solvent type. In this paper, two different diblock copolymers were studied, one block copolymer with small amounts of zinc neutralised sulphonate groups 3.2 mole% chemically bonded on the backbone of polystyrene block and the other block copolymer is without ionic groups. Both the ionic and nonionic block copolymer were dissolved in a polar and selective solvent, i.e dimethylformamide, which is a selectively poor solvent for the second block, poly(*tert*-butylstyrene). We investigate how the presence of small amounts of ionic groups influence fluid rheology, micellar dimensions and number of associated chains per micelle. Measurements were made using viscometry, static and dynamic light scattering in the dilute solution range. One previous study of such a copolymer system on polystyrene-poly(4-vinyl-N-ethylpyridinium bromide) has been done by Gallot *et al*<sup>4</sup>, using a selective solvating solvent for the vinyl-ethylpyridinium bromide block of the copolymer. They showed that the hydrodynamic volume of the micelles is analogous to a star-like micellar model, in which the characteristic lengths of the soluble block of the copolymer influences the size of the micelles, rather than the molecular weight of the micelles.

**TABLE 1:** Molecular characteristics of block copolymer.

polymer	sulphonation level mole%	$M_w/10^5$ g/mole	$\frac{dn}{dc_A}$	$\frac{dn}{dc_B}$	$\frac{dn^d}{dc}$
PS-PTBS	-	1.85	0.206 <sup>c</sup>	0.176 <sup>a</sup>	0.188
SPS-PTBS	3.2	1.85	0.206	0.196 <sup>b</sup>	0.190

a and b values obtained from ref.5 and 6, c measured using Brice-Phoenix refractometer, d calculated from the equation given in the text, A denotes the poly(tert-butylstyrene) block, B denotes the second block, polystyrene or sulphonated polystyrene.

## EXPERIMENTAL SECTION

The two block copolymers used in these studies are polystyrene-b-poly(tert-butylstyrene), designated ps-ptbs and zinc neutralised sulphonated polystyrene-b-poly(tert-butylstyrene) which contained 3.2 mole% sulphonated groups chemically bonded on the polystyrene block backbone, designated sps-b-ptbs. The copolymer has molecular weight 185,000 and polydispersity 1.10 and contains 50 mole% polystyrene. The characteristics of the polymers are listed in table 1.

Polymer solutions using dimethylformamide (DMF) as the solvent were prepared volumetrically using magnetic stirrers for frequent agitation. The stock solutions were stirred for a minimum of 20 hours and then heated in a water bath at 50°C for 6 hours before dilution to ensure complete dissolution. All solutions were filtered through 0.7 μm filters three times prior to use.

### Small angle light scattering

Static and dynamic light scattering measurements were made simultaneously at 20°C using a wavelength  $\lambda_0=496.5\text{nm}$ . The scattered intensities were measured over the angular  $30^\circ$  to  $150^\circ$  in increments of  $10^\circ$ . Measurements were carried out at the Institut für Makromolekulare Chemie of the University of Freiburg, Germany.

### Viscosity measurements

Solution viscosities were measured using standard Ubbelodhe capillary viscometers in a temperature controlled bath at 22°C. The measurements were repeated three times at least and then the average values taken.

## RESULTS AND DISCUSSION

### Static and Dynamic light scattering

The refractive index increment of the homopolymers in DMF were measured using a Brice-Phoenix differential refractometer. The refractive index increment of the copolymer solution can be determined using the equation:

$$\frac{dn}{dc} = W_A \frac{dn}{dc_A} + W_B \frac{dn}{dc_B}$$

where  $w_A$  is the weight fraction of component A,  $dn/dc_A$  and  $dn/dc_B$  are the refractive index increments of components A and B respectively. All  $dn/dc$  values of the homopolymers and copolymers are listed in table 1.

The intensity scattered from a polymer solution in the dilute region can be expressed generally as :

$$\frac{Kc}{R_\Theta} = \frac{1}{M_w} \left( 1 + \frac{q^2 R_g^2}{3} \right) + 2A_2 c$$

Thus from a plot of  $Kc/R$  against  $q^2 + kc$ , the values of  $M_w$ ,  $R_g$  and  $A_2$  can readily be obtained. However, in the case of copolymer solutions<sup>5</sup>, individual homopolymers have different refractive index, composition and polydispersity, thus the equation leads to an evaluation of an apparent molecular weight  $M_{w,app}$  and apparent radius of gyration  $R_{g,app}$ . For both nonionic and ionic containing polymer in DMF, the inverse apparent molecular weight is proportional to the solution concentration with a positive slope related to the second virial coefficient  $A_2$  (figure 1). Extrapolation on the linear plots to zero concentration, and determining the slope and intercept gives  $M_{w,app}$  and  $A_2$  respectively. The  $R_{g,app}$  value can be calculated from the limiting slope of  $(Kc/R)_{c=0}$  versus  $q^2$ . These values are listed in Table 2. Both block copolymer micelles have higher molecular weight than for a single chain. This suggests the presence of a micelle/free chain equilibrium in both solutions which remains overwhelmingly in the favour of micelle formation down to the lowest concentration investigated. However, the ionic micelles are about a factor of two lower in aggregation number. This suggests that the equilibrium micelle size has been reduced by the ionic repulsion between the segments in the corona.

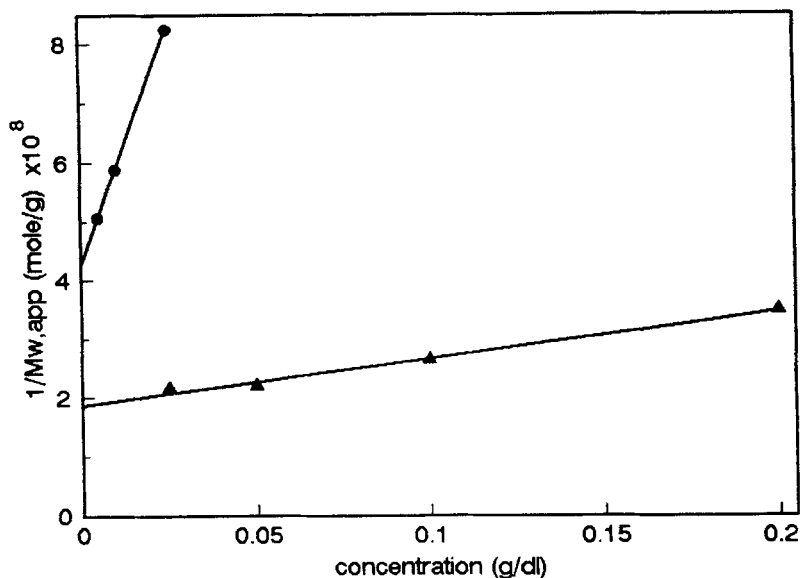


Figure 1: Plots of the apparent molecular weight against solution concentration for PS-PTBS (▲) and for SPS-PTBS (●) in DMF solvent.

**TABLE 2:** Comparison of the micellar radii of sp-ptbs and sps-ptbs diblocks derived from light and viscosity measurements.

Parameters	Nonionic micelles (PS-PTBS)	Ionic micelles (SPS-PTBS)	$R_I/R_N$
$M_{w,app}$ (g/mole)	$5.3 \times 10^7$	$2.2 \times 10^7$	
$R_{g,app}$ (Å)	390	380	1.0
$R_T$ (Å)	927	1379	1.5
$R_H$ (Å)	660	860	1.3
$R_o$ (Å)	500	770	1.5

$R_I/R_N$  indicated ratio of ionic micelle radius to radius of nonionic micelle.

The  $A_2$  value can be related to a thermodynamic radius,  $R_T$ , (excluded volume) based on the equation for a hard sphere<sup>7</sup>;

$$R_T^3 = \frac{3A_2M^2}{16\pi N_A}$$

The values of  $R_T$  calculated from this formula showed that despite their smaller aggregation number ion-containing micelles have much larger dimensions compared to nonionic micelles (Table 2). This indicates that ionic micelles occupy a larger excluded volume especially in the corona due to the solvation of the salt groups resulting in repulsion of like charges (ie. sulphonate groups) along the chain. Note: the static and dynamic measurements are made down to a much lower concentration in order to reach the linear solution range for the ion-containing polymer. This is because the larger effective size reflects a much stronger interparticle interference.

The dynamic light scattering measurements provide information about the hydrodynamic radius of micelles in solution. For spherical particles in infinite dilution, the hydrodynamic radius  $R_H$  can be related to the diffusion coefficient using the Einstein-Stokes relationship<sup>8</sup>:

$$D_0 = \frac{k_B T}{6\pi\eta R_H}$$

In the dilute solution region, both ionic and nonionic micelles showed diffusion coefficients which are independent of concentration. This suggested that both samples have reached hydrodynamic equilibrium down to the lowest concentration investigated. However, the diffusion coefficient of the ionic micelles is smaller than for the nonionic ones. Since the diffusion coefficient is inversely proportional to  $R_H$ , this suggested that a larger hydrodynamic dimension is formed by ionic micelles (figure 2). As we expected, the compact core surrounded by a diffuse sheath stretches out to a greater extent. The formation of such a structure with a very compact core and an extended corona in the ionic micelles is rather analogous to the structure of star molecules, in which the segment density in the shell decreases with increasing distance from the center<sup>9</sup>.

### Viscosity measurements

This distinguishing characteristic of the increase of micelle dimensions with ionic content is further supported by an enhancement of viscosity in

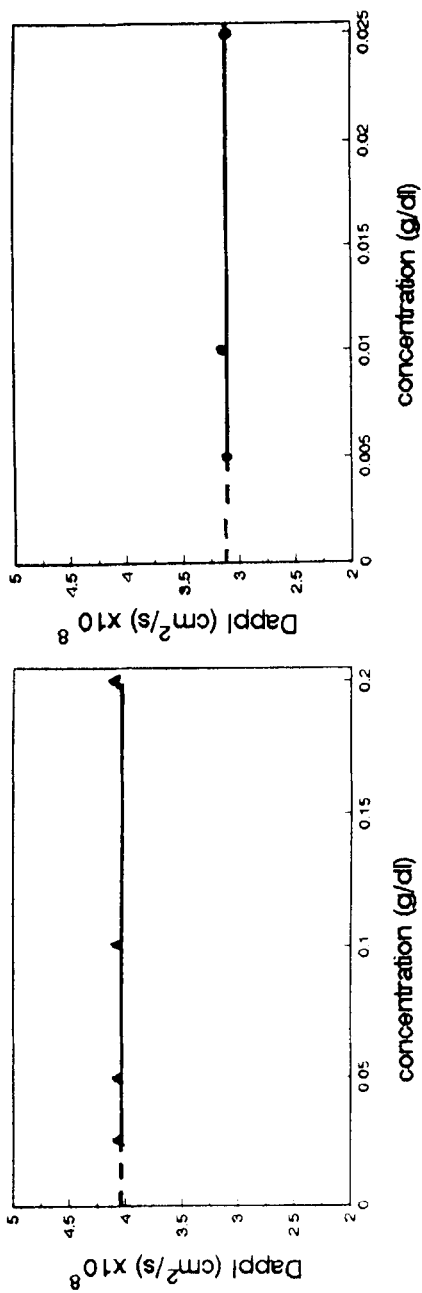


Figure 2: Plot of diffusion coefficient against concentration for samples ps-ptbs (▲) and sps-ptbs (●).



relatively dilute solution (Figure 3). In semidilute solutions, the reduced viscosities of the nonionic micelles is lower than for polystyrene of equivalent molecular weight. However the reduced viscosity of the aggregated micelles with ionic groups is a factor 8 higher than that of the nonionic micelles. For both types of micelle the reduced viscosity remained almost constant as the concentration increases. At the moment, we ignore the upturn at low concentration in the ionomer micelles, and consider only the flat positions of the curve. The upturn behaviour will be discussed below. The intrinsic viscosity can be obtained by extrapolating the reduced viscosity to zero concentration. For a spherical particle, the intrinsic viscosity is directly proportional to the effective hydrodynamic radius  $R_g$  and is given by<sup>10</sup>:

$$[\eta] = \frac{10N_A R_g^3}{M}$$

According to Einstein, the reduced viscosity measures directly the average volume fraction of spherical particles in the system:

$$\eta - \eta_s(1 + 2.5\phi)$$

Hence, this behaviour indicates that the number of particles in the whole system remains constant which is a characteristic of densely packed spherical particles.

In dilute solution, a marked increase in solution viscosity is observed for ion-containing micelles. Such an upturn in reduced viscosity as concentration decreases is typical of polyelectrolyte behaviour. It is also observed for ionomers in polar solvent<sup>11</sup>, as clearly seen in figure 3 where the data for sulphonated polystyrene of the same molecular weight as the copolymer are included. In polar solvent as has already been mentioned, the salt groups are ionised, leaving similarly charged ions attached to the polymer chain. These ionic groups repel each other and hence tend to expand the chain. However, the solvated counterions to some extent screen these charges from each other and reduced the repulsion. As concentration decreases, so does this screening, the repulsion effect increases and chains expand. The expanded rod-like polymers occupy larger excluded volume and hence increase their viscosity. The similar upturn at low concentration for the ionomer and for the ionomer micelles confirmed that the same polyelectrolyte behaviour is occurring in the latter.

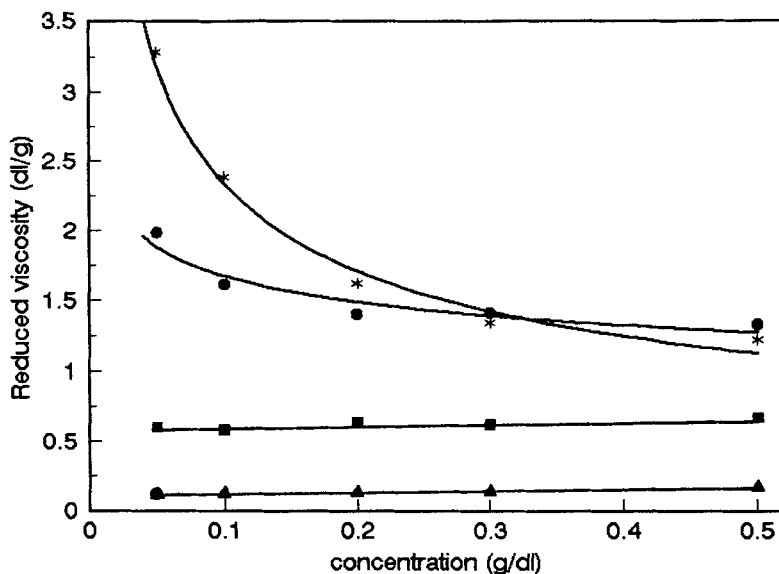


Figure 3: Concentration dependence of reduced viscosity for polystyrene (■), sulphonated polystyrene (\*), PS-PTBS (▲) and SPS-PTBS (●).

### CONCLUSIONS

The lower aggregation number for the ionomer copolymer indicates that the addition of ionic groups has shifted the thermodynamic equilibrium in favour of smaller micelles.

The surface to volume ratio of a sphere increases as the radius decreases. The core volume will be proportional to the number of segments within it, so that the surface area available to an ionic segment emerging from the core will increase as the aggregation number decreases. This demand for a larger footprint on the core may be attributed to repulsive effects between charges on neighbouring copolymers.

The increase effective dimensions observed in the data summarised in Table 2 are probably due to repulsive effects between charges on the same copolymer segment causing expansion of the corona. It is interesting

to note that the  $R_g$  values which are dominated by density are relatively close (though it must be remembered that the smaller aggregation number would suggest an  $R_g$  value of around 290Å). While  $R_T$ ,  $R_o$  and  $R_H$ , all of which reflect interactions, show much larger differences. Thus not only are the ionic micelles expanded, particularly in the corona, but they also, as might be expected, interact much more strongly with each other.

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