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Very weakly charged segmented polyelectrolytes. The effect of coulombic interactions on viscosity and neutron scattering

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Résumé. — Des polymères segmentés de très faible charge (1 charge/100 Å) ont été synthétisés et l'effet des répulsions coulombiennes sur la viscosité et la diffusion des neutrons de leurs solutions aqueuses a été étudié. Un effet polyelectrolyte apparaît dans leur viscosité à des concentrations telles que la longueur d'écran de Debye devienne de l'ordre de la racine carrée de la distance quadratique moyenne entre les charnières chargées. La diffusion des neutrons peut être calculée en utilisant pour la fonction de corrélation directe entre segments $C(r)$ la superposition d'un terme de volume exclu à courte distance $v\delta(r)$ et d'un terme de répulsion coulombienne écrantée $1/r e^{-Kr}$. L'hypothèse d'une conformation consistant, pour grand (faible concentration en polymères, absence de sel) en un alignement de «blobs», apparaît compatible avec les expériences.

Abstract. — Very weakly charged (1 charge/100 Å) segmented polyelectrolytes have been synthesized and the effect of coulombic repulsion on the viscosity and neutron scattering of their aqueous solutions has been studied. A polyelectrolyte effect shows up in the viscosity at concentrations where the Debye screening length becomes of the order of the root mean square distance between charged linkers. Neutron scattering experiments can be fitted to a theoretical segment-segment direct correlation function $C(r)$ which superimposes a classical short range excluded volume term $v\delta(r)$ and a screened coulombic repulsion $1/r e^{-Kr}$. The hypothesis of a conformation consisting of aligned blobs at large screening length (low polymer concentration, no salt) seems compatible with the experiments.

The influence of long range coulombic forces on the scattering factor of rigid spherical objects in low salt solutions is now fairly well understood. The use of neutron and X-ray scattering has allowed one to explore a wide range of scattering vectors covering $R^{-1}$, $K$ and $d^{-1}$, where $R$ is the radius of the sphere, $K^{-1}$ the Debye screening length and $d$ the mean distance between two spheres. Experiments with surface charged spherical particles such as micelles or charged latex show a single peak which can be fitted with existing theories even for very weakly charged systems [1, 2]. A single peak is also observed in the scattering of solutions of highly charged flexible polyelectrolytes in the absence of added salt or at very low salt content. The modeling of such systems is however much more complicated because coulombic interactions not only result in strong interparticle interaction, but in a
stretching of the whole chain as revealed by the increase of the specific viscosity with
decreasing concentration. It is very difficult to work at the extremely low concentrations
required for full extension $\kappa^{-1} \gg 1$, the charged chain contour length, and the situation in the
semi-dilute regime of semi-rigid overlapping chains is theoretically very intricate. Neutron
scattering by mixtures of protonated and deuterated chains of identical nature at different
ratio provide a way to separate experimentally between the intra and interparticle
contribution at any concentration $c_p$ of polymer and $c_s$ of added salt [3, 4]. But the
$c_p$ dependence of the position of the peak cannot yet be deduced from simple Debye type
intersegmental potential [5, 6]. Comparatively very few experiments have been carried out on
very weakly charged flexible systems [7, 8]. Some predictions on their structure have however
been made within the « blob » model [9, 10]. As in the usual case of excluded volume effects
in moderately good solvents, the chain is assumed to retain at short distances i.e. within a blob
its Gaussian statistics and the whole chain statistics is that of a chain of blobs with excluded
volume. In the case of electrostatic interaction the number $g\sigma$ of monomers in a blob is
calculated from the assumption that two charges $a$ interacting at a distance $(g\sigma)^{1/2}$ a have a
repulsive energy of the order of $kT$. In the absence of screening, the chain of « blobs » will
assume an elongated structure. The use of weak polyacids (such as polyacrylic acid) at low pK
or copolymers of charged and uncharged monomers (such as polyacrylamide coacrylic acid)
for such studies can be questioned. In the first case it is known that the pK of the weak acid
will depend on the electrostatic potential produced by other dissociated neighbouring groups
so that the total charge and charge distribution may strongly fluctuate depending on each
chain conformation. Moreover $\kappa^{-1}$ will be limited at low $c_p$ by the concentration of acid
required to control the degree of dissociation. Another fluctuation is involved in the
distribution of charged comonomers in copolymers depending on the reactivity ratio in the
copolymerization process or on the cooperativity or anticooperativity of the hydrolysis
process used to create charged groups by polymer modification. We have for that reason
synthesized and investigated a new type of weakly charged segmented polyelectrolyte
obtained by polycondensation of hydroxyl terminated polyethylene oxide (PEO) with
pyromellitic anhydride. The length of the precursor has been taken large as compared to the
PEO persistence length and comparable with the values of $\kappa^{-1}$ expected for the range of $c_p$
requested by the sensitivity of the experiments. Viscosity measurements have been used to
detect the intramolecular changes of conformation and neutron scattering to study the
combined effect of intra and intermolecular repulsions.

1. Preparation and characterization of the polymers.
$\alpha, \omega$ - diol-polyethylene glycol ($M_w = 2130 \pm 90, \ M_n = 1970 \pm 40,\ [\eta]_{DMF} = 7.23\ \text{cm}^3/\text{gr}$) was reacted with a stoechiometric amount of pyromellitic dianhydride (Fig. 1) in di-
methylacetamide at 80°C. The study of the polycondensation kinetics and the effect of
solvent, catalyst and small deviations from stoechiometry on the average degree of
polycondensation and its distribution will be reported elsewhere. The samples used in this
study have been prepared at exact stoechiometry and fractionated in a benzene-methanol
(50/1)/isooctane mixture. Methanol is thought to decrease by preferential solvation the
possible interactions between carboxylic groups. The molecular weights $M_w$ and mean degree
of condensation $\bar{n}$ measured by light scattering in methanol are given in table I.

Titration of the two carboxylic groups of the diacid linker reveals a small shift in
$P_K$ between the polymers and the micromolecular model derived from pyromellitic dianhy-
dride and 2-ethoxyethanol ($P_K = 3.26$ and 2.97 respectively). There is no polyelectrolyte effect,
i.e. a progressive change of $P_K$ with the degree of dissociation due to the electrostatic potential
of already dissociated neighbouring groups, even in the absence of added tetramethylam-
monium chloride. There is no significant difference in the pK of the two acid functions even in the absence of added TMACl. This precludes to work with one or two charges per linker by changing the pH. The mean charge per unit length or our samples is then ≈ 1 charge/100 Å.

Viscosity measurements reveal that neutral water solutions are stable while acid solutions seem to degrade in the presence of oxygen. The potassium salt resulting from exact neutralisation by KOH (pH 7.55) has been used throughout this work.

2. Viscosity measurements.

Viscosity measurements have been carried out on an Ubbelohde capillary viscosimeter with photoelectric detection. The time of flow t is recorded with an accuracy of $10^{-3}$ s and a reproducibility better than $10^{-2}$ s at 25 °C. The ratio $\eta_{sp}/\eta_{cp} = (t - t_0)/t_0 \cdot \eta_{cp}$ is then plotted as a function of $\eta_{cp}$.

In the presence of an excess of added salt (0.1M KBr) the plot displays the usual linear behaviour

$$\frac{\eta_{sp}}{\eta_{cp}} = [\eta] + k[\eta] \cdot \eta_{cp}$$

with $k = 0.3-0.8$ arising from hydrodynamic interactions. The extrapolated values $[\eta]$ (Tab. II) fit very well with the intrinsic viscosity for uncharged PEO of similar molecular weight calculated according to [11]

$$[\eta] = 0.02 + 2.4 \times 10^{-2} M^{0.73}.$$
Table II. — Intrinsic viscosities $[\eta]$ in the presence of 0.1 M KBr and of the uncharged PEO of same molecular weight and values of $\eta_{sp}/c_p$ at two polymer concentrations $c_p$ in the absence of added salt.

<table>
<thead>
<tr>
<th>$10^{-3}$ M</th>
<th>uncharged</th>
<th>0.1 KBr</th>
<th>$c_p = 20$ g/l</th>
<th>$c_p = 3$ g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4</td>
<td>16.4</td>
<td>22.4</td>
<td>20</td>
<td>19</td>
</tr>
<tr>
<td>14.5</td>
<td>28.2</td>
<td>35.0</td>
<td>38</td>
<td>40</td>
</tr>
<tr>
<td>17.8</td>
<td>32.4</td>
<td>44.1</td>
<td>98</td>
<td>71</td>
</tr>
<tr>
<td>22.0</td>
<td>37.7</td>
<td>47.1</td>
<td>68</td>
<td>91</td>
</tr>
<tr>
<td>28.1</td>
<td>44.4</td>
<td>48.5</td>
<td>72</td>
<td>98</td>
</tr>
<tr>
<td>32.3</td>
<td>49.0</td>
<td></td>
<td>78</td>
<td>109</td>
</tr>
</tbody>
</table>

This shows that the linker has a negligible influence on the chain conformation.

In the absence of added salt however (Fig. 2) the plot displays an upward curvature for the higher $\bar{n}$ at low $c_p$ which is characteristic of polyelectrolytes. The effect indeed disappears when the electrostatic interaction is screened by addition of salt. Several semi empirical expressions have been proposed to linearize the $c_p$ dependence of $\eta_{sp}/c_p$ for highly charged polyelectrolytes. They generally involve some $c_p^{-1/2}$ dependence related to the screening of electrostatic interaction by the polymer itself. We have found that the relation proposed by

![Figure 2](image-url)

Fig. 2. — $\eta_{sp}/c_p$ as a function of $c_p$ for samples of increasing $\bar{n}$ in the absence of added salt. $\bar{n} = 2.8$ (●); 6.3 (○); 7.7 (■); 10.1 (■); 12.1 (△); 13.9 (▲); 7.2 unfractionated (○); lines are guide for the eye.
Yvan Dougherty and Stivala [12]

\[
\frac{\eta_{sp}}{c_p} = \eta_\infty + k^n [\eta]_p^{n-1/2}
\]
surprisingly fits all the results (Fig. 3). Its significance is however not clear.

It should be pointed out that the strong upward deviation of \( \eta_{sp}/c \) takes place at a concentration 15 g/l independent of \( \bar{n} \) which corresponds to a Debye screening length calculated between 38 Å and 22 Å depending whether it is calculated from the concentration of counterions only (1.5 \( \times \) 10\(^{-3} \) M) or taking the linker charges as simple divalent coions. These values can be compared with either the blob size \( D = (\sigma^2 a^4/l_B)^{1/3} \) calculated as explained above with \( a \) the Kuhn length and \( l_B \) the Bjerrum length \( e^2/\varepsilon kT \approx 7.1 \) Å, or the mean square distance between two linkers carrying two charges \( \langle h^2 \rangle^{1/2} = [2 \sigma a^2]^{1/2} \). For a PEO chain of molecular weight 2 000 with a characteristic ratio \( C_\infty = 4 \) [13] the two values \( D = 37.5 \) Å and \( \langle h^2 \rangle^{1/2} = 35 \) Å almost coincide and agree with the higher value of the Debye screening length. On the other hand the study of the sample with \( \bar{n} = 7 \) in solutions with added salt reveals that the deviation at low \( c_p \) completely disappears for \( c_s = 3 \times 10^{-2} \) M, \( \kappa^{-1} = 18 \) Å, close to the lower value.

In any case, at a concentration of 20 g/l in the absence of added salt, which is small enough to remain in the dilute regime, the molecular weight dependence of \( \eta_{sp}/c_p \) should be dominated by weak excluded volume effects. This is clearly seen in the comparison of the Stockmayer-Fixman plot [\( \eta/M^{1/2} = f(M^{1/2}) \) with [\( \eta \)]] extrapolated from data at high \( c_s \) (Tab. II) and a plot of \( (\eta_{sp}/c_p)/M^{1/2} = f(M^{1/2}) \) with \( \eta_{sp}/c_p \) measured at 20 g/l. Both plots are reasonably linear (Fig. 4) and extrapolate at a common value 0.1. From the Flory Fox equation with \( \varphi = 2.5 \times 10^{23} \) one gets \( \langle h^2 \rangle/M^{1/2} = 0.74 \times 10^{-8} \) i.e. \( \langle h^2 \rangle^{1/2} = 33 \) Å for

Fig. 3. — \( \eta_{sp}/c_p \) as a function of \( c_p^{-1/2} \) (same data as in Fig. 2).
$M = 2 \times 10^3$ in fair agreement with the value calculated above. The situation is quite different when using $\eta_{sp}/c_p$ measured at the lowest available $c_p$ (3 g/l). In this case there is a clear jump for $n > 7$ which it is tempting to relate to an increase in the anisodiametry of the conformation as predicted by the model of blob alignment [9].


Small angle neutron scattering studies have been carried out on the spectrometer D17 of the Institute Laue Langevin in Grenoble. ($\lambda = 12$ Å, $q$ range from 0.02 to 0.1 Å$^{-1}$). The sample with $\bar{n} = 10$ has been used throughout since its size is high enough to display an increase in $\eta_{sp}/c_p$ at low $c_p$ and small enough to remain in the dilute regime at $c_p = 15$ g/l, the highest concentration used. Two series of experiments have been performed:

a) at variable $c_p$ (3 → 15 g/l) in the absence of added salt;
b) at two $c_p$ (5 g and 10 g/l) in the presence of added salt ($2 \times 10^{-3}$ to $4 \times 10^{-2}$ M KBr).

The recorded number of counts have been corrected for neutron absorption and normalized to a same number of incident neutrons. The scattering of the solvents has been subtracted from the scattering of the solutions and the results plotted as $I(q)/c_p$ on figures 5, 6 and 7.

The curves can nearly be superimposed at high $q$ irrespective of $c_p$ and $c_s$. This support the idea that the local structure remains unmodified. In the absence of added salt all curves present a flattening or a weak maximum in the intermediate $q$ range whose height increases with decreasing $c_p$. In the concentration domain where the viscosity shows a very minor change (> 10 g/l) we can assume that the radius of gyration remains essentially constant and that the shape of the scattering results mainly from the interactions between undeformed coils. Upon addition of salt this flattening progressively disappears and the intermediate $q$ behaviour merges with the steep increase at low $q$ which is observed in all conditions.

Fig. 4. — $\eta_{sp}/c_p M^{1/2}$ as a function of $M^{1/2}$; $\lim c_p \to 0$ in 0.1 M KBr (Δ); $c_p = 20$ g/l $c_s = 0$ (□); $c_p = 3$ g/l $c_s = 0$ (■).
Fig. 5. — $I(q)/c_p$ as a function of $q$ for different $c_p$, $c_p = 0$: experimental points and calculated curves according to relations 8, 9, 10 with $\langle s^2 \rangle^{1/2} = 40 \text{ Å}$, $A_2 = 1.8 \times 10^{-3}$; $\kappa^2(c_p) = 20 \times 10^{-4} \text{ Å}^{-2}$, $B = 0.4$; $c_p = 15.4 \text{ g/l}$ (□, ------ $c_p = 4/5 C_p$ (×, --→); $c_p = 3/5 C_p$ (○, ---); $c_p = 1/5 C_p$ (*, ⋯⋯). The curve ------ corresponds to $c_p = 1/5 C_p$ with $\langle s^2 \rangle^{1/2} = 50 \text{ Å}$.

From a general point of view, the total scattering factor $S_T(q) = I(q)/I_0(0)$ where $I_0(0)$ is the scattering at $q = 0$ of the solute particles in the absence of interaction can be written as:

$$S_T(q) = P(q) S(q) \propto \frac{I(q)}{c_p}$$  \hspace{1cm} (3)

where $P(q)$ is the solute particles form factor and $S(q)$ the solution structure factor arising from interparticle interactions. By extension of the single contact approximation or RPA [14] for flexible chain molecules, it has been shown that $S(q)$ can be written [5, 6]:

$$S(q) = \frac{1}{1 + nC(q)P(q)}$$  \hspace{1cm} (4)
Fig. 6. \( I(q)/c_p \) as a function of \( q \) for \( c_p = 10 \) g/l and different \( c_s \). Experimental points and calculated curves according to relations (8, 9, 10) with the same parameters as in figure 5; \( c_s = 2 \times 10^{-3} \) (*, ---); \( 6 \times 10^{-3} \) (○, ----); \( 10^{-2} \) (+, ---); \( 4 \times 10^{-2} \) (®, ---).

where \( n \) is the particles number density and \( C(q) \) the Fourier transform of the segment direct correlation \( C(r) \).

In the case of an uncharged polymer \( C(r) \) is taken as \( v \delta(r) \) where \( v \) is the excluded volume. \( C(q) \) is \( q \) independent and relation (4) reduces to

\[
S(q) = \frac{1}{1 + 2A_2 Mc_p P(q)}
\]  

with \( A_2 \) the second virial coefficient.

Since \( P(q) \) is a smoothly decreasing function of \( q \), \( S_T(q) \) presents no maximum.

In the case of a charged chain \( C(r) \) is expected to have a range of the order of the Debye screening length \( \kappa^{-1} \). Values of \( \kappa^{-1} \) relevant to our experiments are given in table III where \( \kappa^{-1} \) has been calculated using in the absence of added salt either the contribution of the counterions only [15] or adding the contribution of the linkers charges on the polymer as...
Fig. 7. — $I(q)/c_p$ as a function of $q$ for $c_p = 5 \text{ g/l}$ and different $c_s$. Experimental points and calculated curves according to relations (8, 9, 10) with the same parameters as in figure 5; $c_s = 2 \times 10^{-3}$ (*, -----); $c_s = 6 \times 10^{-3}$ (□, — — —); $c_s = 10^{-2}$ (+, ..-..); $c_s = 4 \times 10^{-2}$ (○, -----).

Table III. — Values of the Debye screening length $\kappa^{-1}$ relevant to the neutron scattering experiments (the two values correspond to two extreme hypothesis concerning the contribution of the polyelectrolyte charges to the screening), see text.

<table>
<thead>
<tr>
<th>$c_p \text{ g/l}$</th>
<th>$\kappa^{-1} \text{ Å}$</th>
<th>$c_s 10^{-3} \text{ [KBr]}$</th>
<th>$\kappa^{-1} \text{ Å}$</th>
<th>$c_s 10^{-3} \text{ [KBr]}$</th>
<th>$\kappa^{-1} \text{ Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.4</td>
<td>40-23</td>
<td>0</td>
<td>48-28</td>
<td>0</td>
<td>67 -39.6</td>
</tr>
<tr>
<td>12.3</td>
<td>45-26</td>
<td>2</td>
<td>40-26.1</td>
<td>2</td>
<td>49 -34.6</td>
</tr>
<tr>
<td>9.2</td>
<td>52-30</td>
<td>6</td>
<td>31-23.1</td>
<td>6</td>
<td>25 -28.4</td>
</tr>
<tr>
<td>6.2</td>
<td>63-36.4</td>
<td>10</td>
<td>27-21</td>
<td>10</td>
<td>28.7-24.7</td>
</tr>
<tr>
<td>3.1</td>
<td>89-51.4</td>
<td>40</td>
<td>15-13.8</td>
<td>40</td>
<td>15.4-14.4</td>
</tr>
</tbody>
</table>
simple micromolecular divalent coions. The values of $\kappa^{-1}$ match the explored range of $q$ and one expects the structure of $C(q)$ to influence strongly the $q$ dependence of $S(q)$. If $C(r)$ is taken of the Debye type:

$$C(r) \propto \frac{1}{r} e^{-\kappa r}$$

$$S(q) = \frac{1}{Bc_p} \frac{P(q)}{1 + \frac{Bc_p}{\kappa^2 + q^2}}$$

This shape allows for a maximum in $S_T(q)$ but implies that in the absence of added salt all values of $I(0)/c_p$ are equal since $\kappa^2$ is in this case proportional to $c_p$. It doesn't allow for the fast rise of $I(q)/c_p$ at low $q$.

In trying to understand this low $q$ rise we have expanded our measurements at even lower $q$ using light scattering on the same solutions. Strong forward scattering corresponding to very large molecular weights and particle size has been recorded in all cases. All efforts to clear the solution by centrifugation or filtration have failed. Visual inspection of the light scattered reveals that the scattering is dominated by a few very large particles. The situation is not improved by heating. Similar difficulties in the study of water solutions of uncharged PEO have been reported [16, 17]. In what follows we neglect the fast rise at low $q$ and concentrate on the scattering at intermediate and high $q$.

Owing to the segmented character of our polymer we have tried to fit the observed scattering with relation (4) using for $C(r)$ the addition of an excluded volume term $v\delta(r)$ and a coulombic repulsion $1/r e^{-\kappa r}$. This results in:

$$S_T(q) = \frac{P(q)}{1 + \left( \frac{2 A_2 M c + Bc}{q^2 + \kappa^2} \right) P(q)}$$

$P(q)$ has been taken as for a Gaussian chain:

$$P(q) = \frac{2}{u^2} (e^{-u} + u - 1) \quad u = q^2 \langle S^2 \rangle .$$

The radius of gyration $\langle S^2 \rangle^{1/2}$ has been first taken as independent of $c_p$ and $c_s$ and equal to the value 40 Å calculated for a PEO of similar molecular weight $M = 2.2 \times 10^4$. $A_2 = 1.8 \times 10^{-3}$ has been taken from measurements on PEO in water for this molecular weight [18]. $B$ and $\kappa^2$ have been fitted to the best agreement for the scattering by the solution with the highest $c_p = c_{po}$ and $c_s = 0$. $\kappa^2$ has been found equal to $20 \times 10^{-4}$ i.e. $\kappa^{-1} = 22.3$ Å close to the value calculated in table III when taking in consideration the screening by both the counterions and the individual divalent linker charges. $B$, which is related to the polymer charge density, has then been kept constant $= 0.4$ and $\kappa^2$ has been calculated for other concentration according to

$$\kappa^2(c_p, c_s) = \kappa^2(c_{po}) \frac{c_{po}}{c_p} + \frac{[c_s]}{10}$$

where $[c_s]$ is the molar concentration in added salt. The calculated curves are given in figures 5, 6 and 7.
Discussion.

The results for $c_p = 4/5 \ c_{po}$ and $3/5 \ c_{po}$, $c_s = 0$ agree well with experiment and in particular reproduce well the variation of the maximum. At $c_p = 1/5 \ c_{po}$ however the agreement becomes very bad. Since it corresponds to a concentration where $\eta_{sp}/c$ presents an upward deviation we suspect that this could be due to the deformation of the molecule according to the aligned blob model. We have therefore tried to modify $P(q)$. Under our assumption one should not change its high $q$ behaviour which is related to the local statistics but only the low and intermediate $q$ behaviour. As a first attempt we have simply modified $\langle s^2 \rangle$ in relation (9) from 40 to 50 Å. Accordingly, as seen in figure 5 the fit is improved in terms of both the position and height of the maximum but becomes poor at high $q$ as it should. If one assumes ten blobs of diameter $\approx 30$ Å each containing $\approx 2$ charges in the molecule the radius of gyration is expected to vary from $(10/6)^{1/2} \approx 30 \approx 40$ Å for Gaussian statistics to $10.30/\sqrt{2} \approx 86$ Å for full alignment. The viscosity, using the expression for a non draining sphere or an ellipsoid with axial ratio 10 [19] should increase by a factor of 3. At 3 gr/l in the absence of salt the screening length $\kappa^{-1}$ (50-90 Å) remains indeed too small to allow for complete alignment. Experiments are requested with even lower charge densities and lower concentrations.

The fit of the curves in the presence of added salt is less satisfactory. In particular, as soon as the small maximum in the intermediate $q$ region disappears the overlap with the low $q$ scattering which seems to increase with added salt makes the fit much poorer. One should however recall that it is deduced from the fit a $c_s = 0$ with no adjustable parameter. We therefore think that

i) the form taken for $C(r)$ which takes in account both a short range excluded volume and a long range coulombic repulsion is well adapted to the polyelectrolyte behaviour of weakly charged polymeric chains in the explored concentration range;

ii) the results obtained at low $c_p$ in the absence of added salt with both viscosimetry and neutron scattering seems to agree with the hypothesis of blob alignment.

As a final remark it should be stressed that the solution structure factor $S(q)$ influences the high $q$ tail of the scattering in such a way that it approaches a $q^{-1}$ behaviour. Use of a Kratky plot $q^2 I(q)$ as a function of $q$ would lead to erroneous conclusions if interpreted in terms of a varying local stiffness. In our case it is obvious that the local flexibility of the PEO chain is unchanged.

Acknowledgments.

Thanks are due to Pr. M. Benmouna for stimulating discussions on the use and extension of relation (4) and to R. Oberthur our local contact at ILL.

Note added in proof.

One of the referee called our attention to the paper by Lantman [20] and al. who studied weakly charged ionomers in polar solvents along nearly the same lines. They have found the same correlation between the appearance of a polyelectrolyte behaviour in viscosity and the presence of strong intermolecular effects in neutron scattering. Using mixtures of protonated and deuterated polymer molecules, as mentioned in our introduction, they have been able to separate the intramolecular scattering factor and get directly the change of radius of gyration with concentration. Their results can be used for a more complete test of our proposed total scattering law (8) which is now under way.
References