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Small-angle X-ray scattering of poly(acrylic acid) in solution: 1. Dioxane*

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Small-angle X-ray scattering (SAXS) has been applied in obtaining the solution parameters (molecular mass M, radius of gyration R_g, radius of gyration of cross-section R_q, mass per unit length M_u, and persistence length a^*) of a poly(acrylic acid) (PAA) sample in dioxane at 25°C. The M and R_g values measured from SAXS were 552 000 Da (daltons) and 292 Å, respectively. These values are in reasonable agreement with those obtained from solution viscometry measurements on the same sample of PAA in dioxane at 30°C ($M = 567\,000$ Da and $R_g = 227$ Å). The R_q and a^* values obtained from SAXS were 6.1 Å and 14.4 Å, respectively. The M_u value measured from SAXS is 27.9 Da Å^{-1}, in excellent agreement with the model (theoretical) value of 28.6 Da Å^{-1} calculated from the structure and molecular mass of the monomer unit. The length L ($= M/M_u = 19\,790$ Å) obtained from SAXS thus corresponds to the contour length of the molecule and not to the 'hydrodynamic' length (i.e. the length the chain assumes in the fluid medium).

(Keywords: small-angle X-ray scattering; poly(acrylic acid); macromolecular parameters)

INTRODUCTION

The analysis of small-angle X-ray scattering (SAXS) data from dilute polymer solutions yields considerable information about the macromolecular parameters and conformation of a sample in a given solvent[1]. We have used SAXS to investigate the dilute-solution conformation of poly(acrylic acid) (PAA) in dioxane at 25°C. Specifically, we report here the values of the molecular mass, radius of gyration, mass per unit length, radius of gyration of cross-section, and persistence length (M, R_g, M_u, R_q and a^* respectively) for a PAA sample. Solution viscometry measurements were also performed to augment and verify some of the SAXS results.

Studies of the dilute-solution behaviour of PAA in dioxane have been reported from measurements of viscometry and light scattering[2,3]. Those studies established that PAA in dioxane is un-ionized and conforms to the random-coil model. Specifically, Newman *et al.*[2] reported that dioxane is a theta solvent for PAA at 30°C. It is important for us to note that those authors, as well as Flory and Osterheld[3], reported that PAA in dioxane exhibits an 'inverted' phase diagram (that is, a lower critical solution temperature). The solubility of PAA in dioxane thus increases with decreasing temperature. This permits study of PAA/dioxane solutions below the θ temperature without inducing phase separation. The SAXS measurements of PAA in dioxane reported in this work were conducted at 25°C, below the θ temperature.

The purpose of this work is to examine the macromolecular parameters and conformation, from SAXS and viscometry, for PAA in dioxane below the θ temperature. These results will be compared with those obtained for the same sample of PAA in water in a following paper[4].

THEORETICAL

The theoretical basis of SAXS has been reviewed[1]. In this section, we capture the relevant theoretical approaches utilized in deriving macromolecular parameters from the measured scattering curves.

The molecular mass is determined from:

$$M = \frac{21.0[I(0)/c]_0 a^2}{I_0(z_2 - v_2\rho_1)^2 d} \tag{1}$$

where $I(0)$ is the scattered intensity extrapolated to zero scattering angle (i.e. zero scattering vector); c is the sample concentration (g cm^{-3}); $[I(0)/c]_0$ is their ratio extrapolated to zero concentration; a is the sample-to-detector distance (cm); d is the sample thickness (cm); 21.0 is a combination of various experimental constants; and I_0 is the incident X-ray beam energy. The factor $(z_2 - v_2\rho_1)^2$ is the absolute electron density contrast between solvent and solute, where ρ_1 is the electron density of the solvent (mol electron cm^{-3}), z_2 is the number of moles of electrons per gram of solute and v_2 is the partial specific volume of the solute (cm^3 g^{-1}).

The R_g value is obtained by application of the Guinier

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[*] This paper is dedicated to the memory of Professor R. D. Andrews, colleague and friend. This paper is taken, in part, from the dissertation submitted by T.J.T. to the faculty of Stevens Institute of Technology in partial fulfilment of the requirements for the degree of Doctor of Philosophy

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equation[1] to the scattered intensities:

$$I(q) = I(0)\exp(-q^2R_g^2/3) \qquad (2)$$

where q is the scattering vector, $q = (4\pi/\lambda)\sin\theta$, λ is the X-ray wavelength (1.54 Å) and the scattering angle is 2θ.

A plot of $\ln I(q)$ vs. q^2 (Guinier plot) is constructed and the radius of gyration is calculated from the slope of the linear, innermost portion of the curve, while $I(0)$ is taken from the intercept. Values of R_g and $I(0)$ are obtained for various concentrations and are extrapolated to $c = 0$ to obtain these parameters in the absence of interparticle interference.

For elongated particles, Porod (Ch. 2 of ref. 1) has shown that the outer portion of the scattering curve takes on a characteristic functional dependence, due to the cross-section of the particle, namely:

$$I(q) = \mathscr{L}\pi I_c(q)/q \qquad (3)$$

where $\mathscr{L}$ is the length of the scattering particle and $I_c(q)$ is the scattered intensity arising from the cross-section of the particle. It is not necessary that the entire particle be elongated to observe this type of behaviour; even a randomly coiled polymer may be viewed as a connected sequence of elongated segments. Since the behaviour of the outer portion of the curve is due to the cross-section of the particle, analysis of the scattering curve in this region yields information regarding the cross-sectional dimensions and mass per unit length of the particle. If the cross-section measured is that of the polymer contour (i.e. backbone), then $\mathscr{L}$ is equal to L, the contour (or stretched) length of the molecule ($L = M/M_u$). This has been demonstrated by Stivala and coworkers in their studies of a variety of linear and branched (e.g. star) polymers in solution[5–8].

The R_q value is determined from an equation analogous to equation (2):

$$I_c(q) = I_c(0)\exp(-q^2R_q^2/2) \qquad (4)$$

where $I_c(q) = I(q)q$, a factor of $\mathscr{L}\pi$ cancelling from each side of the equation. As with the radius of gyration, the radius of gyration of the cross-section is calculated from the slope of a plot of $\ln I_c(q)$ vs. q^2 (Guinier plot of the cross-section factor). Since the cross-sectional parameters are derived from scattered intensities at high scattering vectors, they are not affected by interparticle interference and do not have to be corrected by extrapolation to $c = 0$.

The mass per unit length (M_u) is calculated from:

$$M_u = \frac{6.69[I_c(0)/c]_0 a^2}{I_0(z_2 - v_2\rho_1)^2 d} \qquad (5)$$

The value of $I_c(0)$ used in equation (5) can be measured in one of two ways. One could extrapolate the Guinier plot of the cross-section factor to evaluate it. Conversely, a linear plot of the cross-section factor could also be used. Such a plot would tend, at high values of q, to a constant, or 'plateau', giving the value of $I_c(0)$ as the value of the curve in the plateau region. The latter technique is preferred when the plateau region occurs at very high values of q (e.g. $q > 0.015$), making accurate extrapolation to the logarithmic axis of the Guinier plot difficult. This technique is utilized in the present work.

Inspection of equations (1) and (5) reveals:

$$[I(0)/c]_0 = (M\pi/M_u)[I_c(0)/c]_0 \qquad (6)$$

Thus, we can calculate the extrapolated zero-angle intensity from the extrapolated value of the cross-section factor, provided M and M_u are known. This is useful if data in the Guinier region cannot be obtained to sufficiently low angles to allow for accurate extrapolation (e.g. if the particle is very large). However, M must be estimated from some independent technique.

The final macromolecular parameter discussed in this work is the persistence length a^*. The persistence length, originally defined by Kratky and Porod[1], is the average length that a polymer in solution persists in a given direction. As such, it may be taken as a measure of the stiffness of the chain. The value of a^* is calculated from SAXS data from the transition point between chain scattering and rod scattering as determined from the Kratky plot (persistence length plot), a plot of $I(q)q^2$ vs. q. This transition point occurs at a characteristic q value, q^*; a^* is calculated from q^* by:

$$a^* = (1/K)(\lambda/2\theta^*) \qquad (7)$$

where $2\theta^*$ is calculated from q^*. The constant K has been given values ranging from 2.19 to 3.29 by several authors[9–11]. In this work, we offer an average value of a^* computed with an average value of K equal to 2.74. The extremes of a^* calculated based on the diversity of values for K do not greatly affect the numerical results, nor the general conclusions, of this work. The persistence length plot is not concentration-dependent[1].

EXPERIMENTAL

Materials

Poly(acrylic acid) (PAA) was purchased from Polysciences Inc. The material had a nominal molecular mass of 450 000 Da. 1,4-Dioxane was purchased from Aldrich (Gold Label) and purified to remove absorbed water by refluxing over sodium followed by distillation.

Methods

Solution viscometry. Relative viscosities, η_r ($= t/t_0$ for dilute solutions, where t_0 and t are the efflux times of solvent and solution of concentration c, respectively), were determined at 25 and 30°C for various concentrations in Ubbelohde viscometers. Calculation of the intrinsic viscosity, $[\eta]$, of the PAA in solution was accomplished by double extrapolation of the plots of η_{sp}/c and $\ln(\eta_r)/c$ to $c = 0$ according to Huggins' equations[12], where $\eta_{sp} = \eta_{r-1}$.

Small-angle X-ray scattering. SAXS measurements were conducted on a Kratky camera with an extended flight path[13] and utilizing a 20 μm entrance slit in conjunction with a one-dimensional position-sensitive proportional counter (TEC, model 205) operated at bias voltage of +1900 V. The bias voltage provides a spatial resolution of 100 μm, which, in conjunction with the entrance slit, allows for a lower limit of the scattering angle of 0.8 mrad (or a Bragg value of approximately 2000 Å). X-rays were generated with a stabilized Siemens Krystalloflex generator operated at 40 kV and 30 mA and a Siemens tube fitted with a Cu target. A nickel filter in combination with energy discrimination in the detector ensured measurement of only those X-rays of 1.54 Å wavelength.

X-ray intensity (I) was measured as a function of scattering vector (q). The measured intensity values were corrected for sample transmission, parasitic scattering, detector sensitivity, solvent scattering, statistical fluctuation (smoothed by multiple regression) and electron density inhomogeneity (Porod–Luzzatti correction). The resulting I vs. q curves were then corrected for collimation error ('desmeared') using the computer program of Glatter[14]. Incident intensity (primary beam energy), I_0, necessary for determination of mass parameters, was measured using a Lupolen standard scatterer[15].

Partial specific volume. Partial specific volume (v_2) was calculated from density measurements according to:

$$v_2 = \frac{1}{\rho} - \frac{1}{\rho^2}(1 - \omega_2)\frac{\partial\rho}{\partial\omega_2} \qquad (8)$$

where ρ is its density and ω_2 the weight fraction of the solution. Density measurements were conducted on a digital precision density meter (Anton Paar KG). The v_2 of PAA was determined to be 0.643 cm^3 g^{-1} in dioxane at 25°C.

Electron density contrast. The absolute electron density contrast (i.e. the excess moles of electrons per gram of solvent, squared) was calculated as the squared difference between the electron density of the solute and the electron density of solvent displaced by the presence of the solute, $(z_2 - v_2\rho_1)^2$. Here, ρ_1 is the electron density of the solvent, that is, the moles of electrons per cubic centimetre of the solvent and z_2 is the number of moles of electrons per gram of solute. The value thus calculated is 0.0313 for PAA in dioxane.

RESULTS

Figure 1 shows the Guinier plots for PAA in dioxane (at 25°C) at the three concentrations indicated. The intercepts and slopes of the linear, low-angle regions of these plots are used to calculate the M and R_g values, respectively, according to equations (1) and (2).

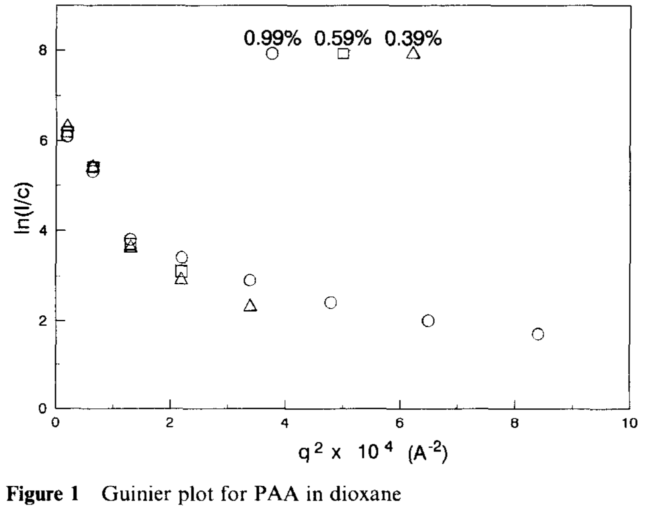

Figure 1 Guinier plot for PAA in dioxane

Figure 2 is the plot of R_g vs. concentration. The extrapolation of R_g to $c = 0$ yields the value in the absence of interparticle interference.

Figure 3 is the Guinier plot of the cross-section factor for PAA ($c = 9.9$ mg cm^{-3}), according to equation (4). The slope of the outermost, linear region of the curve is used to calculate the R_q. As stated earlier, the cross-section parameters do not require extrapolation to $c = 0$.

Figure 4 is a linear plot of the cross-section factor for

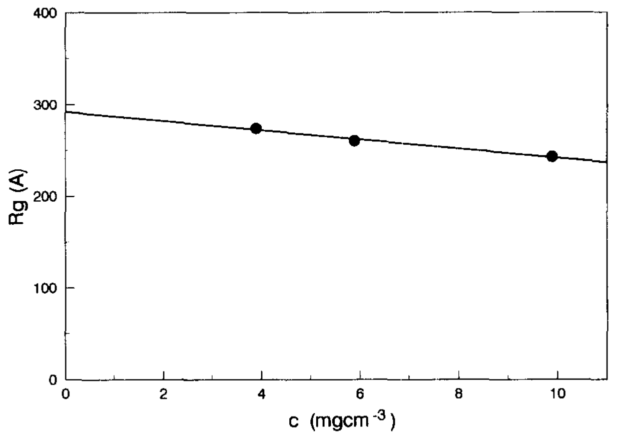

Figure 2 Radius of gyration vs. concentration

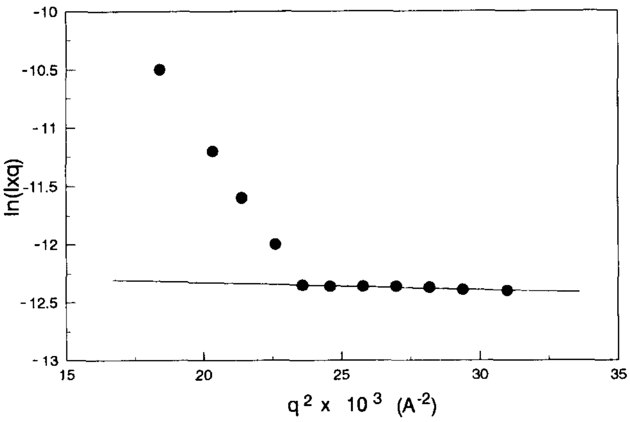

Figure 3 Guinier plot of cross-section factor for PAA in dioxane, $c = 0.29\%$

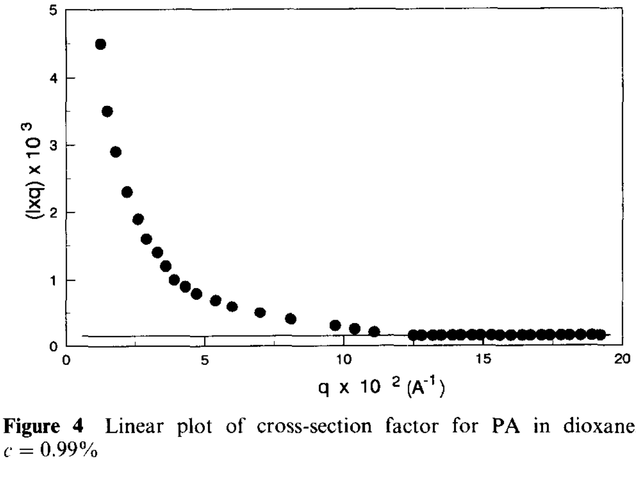

Figure 4 Linear plot of cross-section factor for PA in dioxane, $c = 0.99\%$

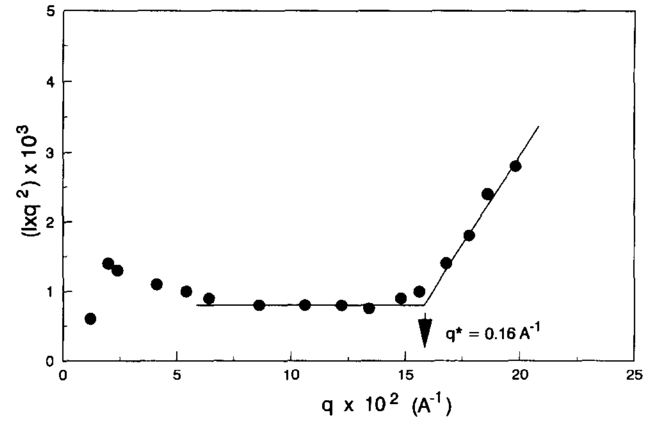

Figure 5 Persistence length plot for PAA in dioxane, $c = 0.99\%$

PAA ($c = 9.9\,\mathrm{mg\,cm^{-3}}$), from which $I_c(0)$ is obtained for calculation of M_u according to equation (5). The a^* value is obtained for PAA ($c = 9.9\,\mathrm{mg\,cm^{-3}}$) from *Figure 5* and equation (7). *Table 1* summarizes the SAXS and intrinsic viscosity data of PAA in dioxane.

A brief discussion of the errors in the viscometry and SAXS measurements is in order. The viscometry data were measured twice and were found to agree within 5%. The averaged results are reported in this work. SAXS scattering curves were measured twice and found to agree within 10%. Average scattering curves were then constructed for calculation of the SAXS parameters. All linear extrapolations (e.g. viscometry data, Guinier plots and extrapolations to $c = 0$) were done by linear least-squares and the fit was excellent in all cases ($r^2 > 0.99$).

DISCUSSION

The values of M obtained from viscometry (30°C) and from SAXS (25°C) in dioxane are in good agreement. The supplier lists a value of $M = 450\,000$ Da (nominal) for this sample. Close examination of the viscometry data in dioxane[16] did not reveal any non-linearities (i.e. polyelectrolyte behaviour) and the data are similar to those reported elsewhere for samples of similar molecular masses. (For example, Newman *et al.*[2] reported intrinsic viscosities of 0.479 and $0.715\,\mathrm{dl\,g^{-1}}$ for PAA samples with molecular masses of 405 000 and 768 000 Da, respectively, in dioxane at 30°C.) Thus, SAXS has been measured to sufficient resolution in dioxane to provide accurate extrapolation of the Guinier plots and calculation of M.

Dioxane is a θ solvent for PAA at 30°C and the dioxane–PA system displays a lower critical solution temperature. Thus, PAA in dioxane at 30°C is in the unperturbed random-coil conformation[2,12]. Viscometry data measured at 30°C were used to calculate R_g by application of the Flory–Fox[12] equation:

$$[\eta] = \Phi\langle r^2\rangle^{3/2}/M \qquad (9)$$

where $\langle r^2\rangle^{1/2}$ is the root-mean-square end-to-end distance and $\langle R_g^2\rangle = \langle r^2\rangle/6$ for the randomly coiled polymer chain. Φ is the 'universal' constant for random coils, ranging from 2.1×10^{21} to 2.5×10^{21} for units of $[\eta]$ and r in $\mathrm{dl\,g^{-1}}$ and cm, respectively[12]. We have used the value of 2.1×10^{21} based on the work of Newman *et al.*[2]. The R_g thus obtained is 227 Å compared with the value of 292 Å measured from SAXS (cf. *Table 1*). It should be noted that the SAXS R_g (25°C) is greater than the viscosity R_g (30°C). Notwithstanding any sensitivity differences in measurement between $[\eta]$ and SAXS, this is not surprising since PAA in dioxane exhibits a lower critical solution temperature. In effect, the solubility increases with decreasing temperature (i.e. dioxane becomes a 'better' solvent with decreasing temperature, thus perturbing the conformation from the ideal, unperturbed random coil). On moving from the unperturbed state at 30°C (θ temperature) to the perturbed state at 25°C, the chain undergoes an isotropic expansion[12,17]. Hence, the R_g should be larger at 25°C than at 30°C. This behaviour is reflected in the higher $[\eta]$ at 25°C *versus* that at 30°C (cf. *Table 1*).

The isotropic expansion factor, α, is calculated from the Flory–Fox[17] equation:

$$\alpha^3 = [\eta]/[\eta]_\theta \qquad (10)$$

where $\alpha = \langle r^2\rangle^{1/2}/(\langle r^2\rangle^{1/2})_\theta = \langle R_g^2\rangle^{1/2}/(\langle R_g^2\rangle^{1/2})_\theta$. θ referring to the unperturbed dimension. The value of α is 1.20, indicating a slight expansion of the chain on going from 30 to 25°C. Calculation of the radius of gyration of the slightly perturbed random coil, by application of equation (10) to the viscometry data obtained at 25°C, yields a value of 272 Å, in reasonable agreement with the value of 292 Å obtained from SAXS. Kurata and Yamakawa[18] modified equation (10) for systems close to the θ point:

$$\alpha^{2.43} = [\eta]/[\eta]_\theta \qquad (10a)$$

Using equation (10a), $\alpha = 1.25$, we calculate $R_g = 284$ Å, which is in slightly closer agreement with the experimental value of 292 Å obtained from SAXS.

The low value of the persistence length, $a^* = 14.4$ Å at 25°C (cf. *Table 1*), for PAA in dioxane implies that the chain does not persist in a preferred direction for a large number of monomer units. This implies that the chain is quite flexible, in accord with the random-coil conformation. This value of a^* compares favourably with other random-coil polymers. For example, Tricot[19] reports $a^* = 12$ Å for aqueous sodium polyacrylate in highly concentrated NaBr calculated by application of viscometric theories; Muroga *et al.*[22] report $a^* = 8$ to 15 Å for

Table 1 Solution parameters of PAA in dioxane

T (°C)	$[\eta]$ (dl g^{-1})	M (Da)	R_g (Å)	M_u (Da Å^{-1})	R_q (Å)	a^* (Å)	L (Å)
25	1.10	552 000[a]	292[a]	27.9[a]	6.1[a]	14.4[a]	19 790[a]
30	0.64	567 000[b]	227[c]				

[a] From SAXS
[b] Calculated from the $[\eta]$–M relation[2]
[c] Calculated from equation (9)

β-substituted and unsubstituted polyacrylates by SAXS (poly(t-butyl acrylate) and poly(t-butyl methacrylate)) in toluene; Stivala *et al.*[9] report $a^* = 21.1$ Å for heparin in the random-coil conformation by SAXS.

The persistence length has been related to R_g and L (the contour or stretched length) for randomly coiled polymers by Benoit and Doty[21]. For molecules with $L/a^* \gg 1$, the relation reduces to:

$$R_g = (La^*/3)^{1/2} \qquad (11)$$

Substitution of the values of L and a^* from SAXS yields $R_g = 308$ Å, which is in good agreement with the direct experimental value of 292 Å. This supports, as in earlier papers[5–8], that L is, in this case, the contour (stretched) length of the molecule and not the hydrodynamic length, i.e. the length of the macromolecule in the fluid medium (e.g. the length of a helix).

The model (theoretical) mass per unit length of the chain can be calculated from the molecular mass of the monomer unit, M_0, and the length of the monomer unit, h_0, by:

$$(M_u)_{th} = M_0/h_0 \qquad (12)$$

For PAA, $M_0 = 72$ Da and, from a calculation based on bond lengths and angles[16], $h_0 = 2.52$ Å. From equation (12), we calculate $(M_u)_{th} = 28.6$ Da Å^{-1}. This is in excellent agreement with 27.9 Da Å^{-1}, obtained from SAXS, in dioxane. The agreement between the theoretical and experimental values of the mass per unit length supports that the L calculated from SAXS data ($= M/M_u$) is the contour length for the randomly coiled PAA molecule in dioxane.

The value of M_u for PAA in dioxane was not reported in prior work. Values of R_q, the radius of gyration of cross-section, have been reported for PAA derivatives by other authors. Muroga *et al.*[20] reported that R_q values ranged from 4 to 7 Å for several polyacrylates in random-coil conformations in toluene from SAXS. Tricot[19] studied sodium polyacrylate in water with added salt and reported R_q values of 4 to 6 Å by application of viscometric theories of rigid chains. These values are in good agreement with the value of 6.1 Å reported in this work.

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