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Analysis

Dynamic Light Scattering from Dilute and Semi-Dilute Water Soluble Flexible Polymer Solutions

Polyacrylamides in the Presence of Salt

Guy Muller

ERA 471 du CNRS "Polymères, biopolymères, membranes", Laboratoire de chimie macromoléculaire, Faculté des Sciences de l'Université de Rouen-Haute Normandie, 76130 Mont Saint Aignan, France

SUMMARY

Low angle quasi-elastic light scattering has been used to measure translational diffusion coefficients of sodium salts of partly hydrolyzed polyacrylamide samples in the presence of added NaCl. Experiments have been performed both in the dilute concentration range and above the critical concentration for overlapping of polymeric chains. The results reported in the semi-dilute domain are in agreement with the scaling laws predicting the concentration dependence of diffusion coefficients of flexible coils in good solvent condition.

INTRODUCTION

Dynamic light scattering which probes local concentration fluctuations in solution provides an accurate procedure for measuring polymer diffusion coefficients and useful data concerning the macromolecular dynamics are thus obtained. Furthermore combination with data obtained from classical static light scattering measurements is of interest for the characterization of macromolecules (ratio between the radius of gyration and the hydrodynamic radius) (1). As compared to the case of neutral polymer solutions at both good and ϕ solvent conditions (2-7), data concerning static and dynamic phenomena in dilute and semi-dilute polyelectrolyte solutions are more limited (8-12). Here we want to present data concerning the diffusion behaviour of polyacrylamide solutions which can be considered as a good example of flexible hydrosoluble polymers, the ionic character of which may be varied by changing the extent of hydrolysis (13,14). The effect of polymer concentration C_p, molecular weight $\bar{M}_w$ and salinity C_s is reported.

EXPERIMENTAL

Methods. Static light scattering measurements were performed both at wide angle (30-150°, FICA) and at low forward angle (5°, CHROMATIX KMX6). For dynamic experiments the Chromatix KMX6 low angle laser photometer is equipped with a real time, multibit 64 Channel Autocorrelator (MALVERN K7025). Scattered light is collected at low angle (5°) and then focused through an aperture (10-50 µm in diameter) on to the photomultiplier. The photopulses are passed through a discriminator amplifier to the computer controlled correlator where they are treated to calculate the autocorrelation function of the scattered light (homodyne mode detection). The average time constant is directly related to the translational diffusion coefficient D_t (or the hydrodynamic radius R_h) by $\Gamma(K)=2D_tK^2$ (K is the scattering vector).

Polymer samples. Low molecular weight (LMW) and high molecular weight (HMW) partly hydrolyzed (30% COONa) polyacrylamide under Na form were investigated in the presence of added NaCl (2 and 20 g/l). The two samples have the

same spacing between the ionic groups along the contour length (b=8,3 Å) and the dimensionless charge density parameter is λ=0.86. All solutions were filtered through Millipore or Nucleopore of different pore sizes depending on the polymer samples and on the concentration.For each sample several concentrations were prepared below and above the critical concentration C^x for overlapping of polymeric coils roughly defined as $C^x \sim M_w/R_g^3 N_a$ (R_g is the radius of gyration).
The molecular characteristics of polymer samples are given in Table I and in Figure 1.

TABLE I

Characteristics of the Polyacrylamide samples

SAMPLE	HMW	LMW	
Salinity	NaCl 20g/l	NaCl 2g/l	NaCl 20g/l
M_w	$8\ 10^6$	$1.6\ 10^5$	
$[\eta]$ ml/g	3800 (1)	242	130
A_2 cm^3 g^{-2} (2)	$6\ 10^{-4}$	$6\ 10^{-3}$	$1.6\ 10^{-3}$
$(R_g)_z$ cm	$2\ 10^{-5}$(3) $2.4\ 10^{-5}$(4)	$2.4\ 10^{-6}$(3)	$1.8\ 10^{-6}$(3)
$(R_h)_z$ cm	$1.5\ 10^{-5}$(5)	-	$1.3\ 10^{-6}$(5)

(1) intrinsic viscosity at low shear rate (10 s^{-1} Contraves)
(2) second virial coefficient obtained from the concentration dependence of the scattered light in the limit of zero scattering angle (Fig.1c)
(3) radius of gyration calculated through Fox-Flory relation
(4) radius of gyration obtained from the angular dependence of the reciprocal scattered light at infinite dilution (Fig.1a)
(5) obtained from the measured diffusion coefficient extrapolated at infinite dilution (Stokes-Einstein equation)
(2') as indicated in Fig.1b at $C>C^x$ an upward curvature is observed due to the influence of the third virial coefficient.

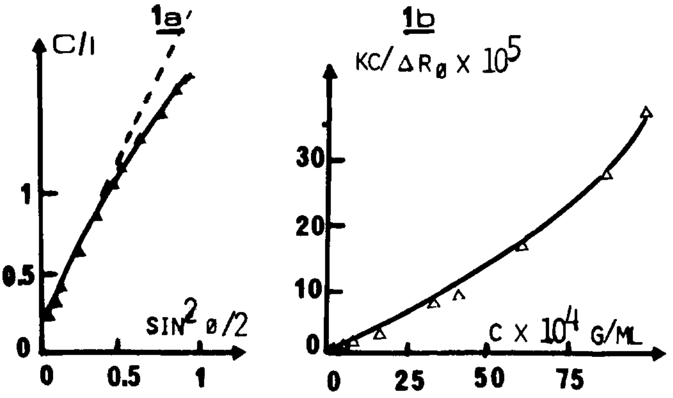

Figure 1. Angular dependence of the reciprocal intensity function at zero concentration for the HMW sample in the presence of 20g/l NaCl (Fig.1a) and concentration dependence (scattering angle=5°) of the scattered light for semi-dilute LMW sample in the presence of 2 g/l NaCl (Fig.1b).

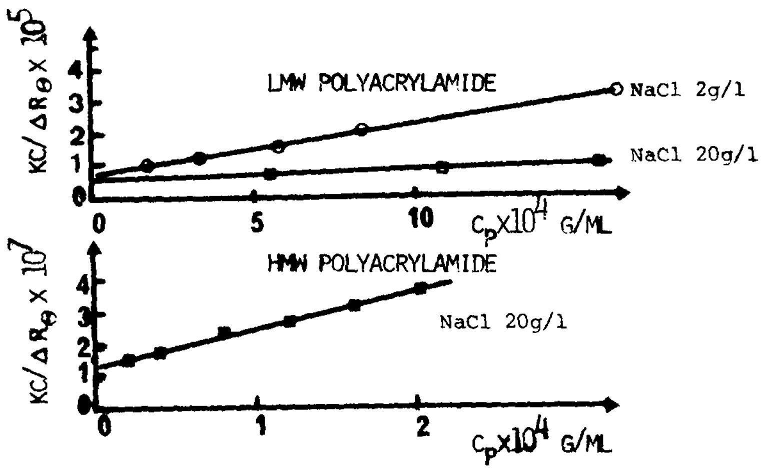

Figure 1c. Concentration dependence (scattering angle=5°) of the scattered light in the dilute regime.

RESULTS AND DISCUSSION

In Figure 2 is reported the concentration dependence of the measured diffusion coefficient D_t for the polymer samples.Obviously two different diffusion behaviours are evidenced.Whereas in the low concentration range D_t is observed only slightly changing with the polymer concentration C_p an increase of D_t vs. C_p is observed in the concentration domain where local intermolecular interactions become important.At constant charge density the C_p for which the individual chains start to overlap is found both $\bar{M}_w$ and salinity dependent.As expected at constant charge density and $\bar{M}_w$ the critical concentration is only dependent on the extent of added salt i.e. on the extension state of polymeric coils.

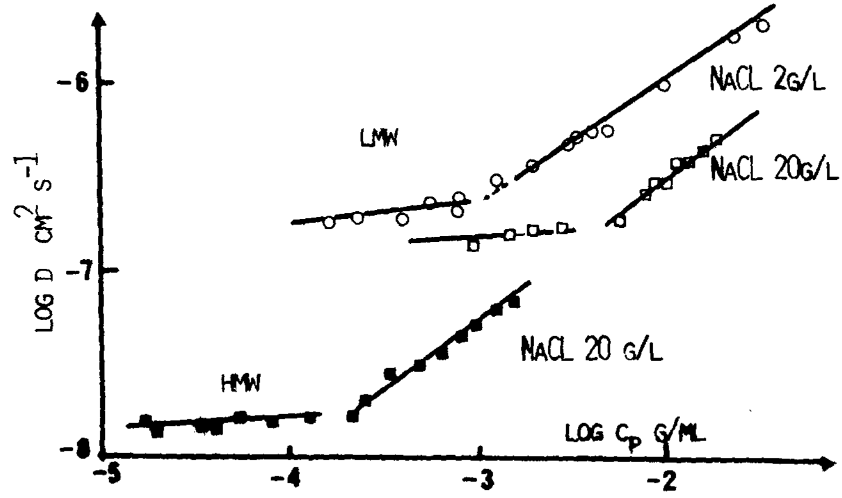

Figure 2. Concentration dependence of the diffusion coefficient for LMW and HMW partly hydrolyzed polyacrylamides in good solvent conditions

In the dilute concentration range, the concentration dependence of the diffusion coefficient can be approximated by a series expansion of the form $D_{(C)}=D_0(1+K_D C_p)$ where D_o is obtained by extrapolation of the measured D_t at infinite dilution and is related to the hydrodynamic radius through the Stokes relation. Both thermodynamic and hydrodynamic factors are included in K_D which is formulated as $K_D=2A_2\bar{M}_w-\bar{v}_2-K_f$, wherein K_f, the hydrodynamic interaction parameter of the frictional coefficient, is dependent on both intra- and intermolecular forces. In θ condition, $K_f=0$; since in such condition the virial coefficient A_2 is zero, a weak concentration dependence of D_t is expected. On the contrary for polyacrylamide samples investigated here, good solvent conditions prevail as indicated by the values of virial coefficients and also by the relation found between viscosity and molecular weight ($\eta \sim M_w^{0.8}$;unpublished results) in the presence of 20g/l NaCl) thus explaining the observed concentration dependence of D_t.

In dilute concentration domain, the hydrodynamic radii R_h are observed of the same order of magnitude than the radii of gyration thus indicating that the dominant parameter governing the diffusion behaviour is the averaged dimension of isolated polymeric chains (TABLE II)

TABLE II

Polyacrylamide in the presence of 20g/l NaCl

Sample	$10^7 D_t(c\to o)$	$R_h=kT/6\pi\eta D_t$ (cm)	K_D(ml/g)	$(R_g)_z$ (cm)
HMW	0.14	$1.5\ 10^{-5}$	1370	$2\ 10^{-5}$(F.Flory) $2.4\ 10^{-5}$(Zimm plot)
LMW	1.6	$1.3\ 10^{-6}$	97	$1.6\ 10^{-6}$(F.Flory)

The relationship between R_h and R_g has been recently reviewed (15); in all cases R_h is reported smaller than R_g as it is also observed here. From our experiments, the following relation is found:

$$R_h \simeq 0.7_3\ R_{g(F.F.)} \simeq 0.6_3\ R_{g(L.S)}$$

$R_{g(F.F)}$=calculated according the Fox-Flory relation

$R_{g(L.S)}$=measured from angular dependence of scattered light.

As shown in Figure 2, the measured diffusion coefficient is observed to increase with C_p in the concentration range where the chains are interpenetrating and therefore local intermolecular interactions become important (semi-dilute domain). It is found that D_t increases with the polymer concentration according to a power law with an exponent found near 0.7 (for both samples and the salinity investigated here) which is in rather good agreement with the concentration dependence predicted from scaling arguments for flexible polymer chains in good solvent conditions (16).
As theoretically predicted, above C^x the measured diffusion coefficient is found molecular weight independent thus indicating that the fluctuations probed by quasi-elastic light scattering are due to cooperative modes of interpenetrating chains (cooperative diffusion) with a characteristic length (dynamic correlation distance) much smaller than the chain radius of gyration and corresponding to the average distance between entanglements. Further work is in progress and we have observed scaling relations for semi-dilute unhydrolyzed polyacrylamides with lower values for the exponent although good solvent conditions also prevail in such a case (unpublished results) (17).

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