

Molecular Weight Determination of an Optically Active Polysulfonamide (PLL) Synthesized by Interfacial Polycondensation

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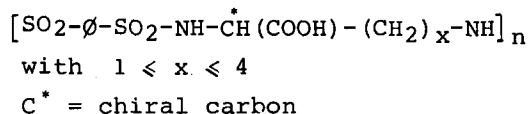
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Summary

In order to study their molecular weight, optically active polysulfonamides were investigated by light scattering and viscosity measurements. The corresponding MARK-HOUWINK type relation is established.

Introduction

New optically active polysulfonamides were prepared in our Laboratory (2,5a) by condensation of 1,3-benzene disulphonyl chloride and some L-diaminoacids. These polymers -which are not stereoregular- have the following structural unit :



Some other derivatives were obtained by their partial or total N,N' methylation (2,5a).

Their conformational properties in water have been largely described (3,4,6,7,8,15,16,17,19). Particularly in the case of the polycondensate of 1,3-benzene disulphonylchloride and L-lysine (PLL) we were interested (5b, 9) in testing the suitability of theoretical models of polyelectrolyte chains (equivalent spherical models of LINDERSTRØM-LANG (12) and HERMANS, OVERBEEK (1)): this requiring the knowledge of the polyelectrolyte molecular weight.

Furthermore, it was of interest to obtain a better characterization of these new polymers, by establishing a relationship between intrinsic viscosity and molecular weight (MARK-HOUWINK type relation), particularly as few corresponding data have been proposed for polysulfonamides.

Experimental

Materials

The synthesis and characterization of PLL (and other related polysulfonamides) were already described (2,5a).

Fractionated samples of PLL were obtained by coacervation, according to the method of MEFFROY-BIGET (13), from the ethyl ester of PLL (PLL_E) in dimethylformamide-ethyl alcohol mixtures. The final fractions of PLL_E were hydrolyzed to obtain corresponding fractions of PLL, as in the general synthesis procedure (2).

MEASUREMENTS

- viscometric measurements were performed as reported in (7) with a Fica viscomatic viscometer.
- the refractive index increments dn/dc measurements were carried out with a Brice-Phoenix Differential Refractometer at $\lambda = 546$ nm and $t = 25^\circ\text{C}$
- light scattering measurements were performed with a Fica photogoniometer model 42 000.

Solutions were made dust-free by centrifugation (5h, 20,000 g). The effectiveness of this clarification was satisfactory as shown from the dissymetry values observed for the solvent ($I_{45}/I_{135} = 1,1$).

Molecular weights for fractionated and unfractionated samples of PLL were calculated according to ZIMM and/or DEBYE methods.

Results and Discussion

Unfractionated samples of PLL

Refractive index increments for PLL in different solvents are given in table I

Table I

Refractive index increments for PLL ($\lambda = 546$ nm, $t = 25^\circ\text{C}$)

Solvent	dn/dc (ml g^{-1})	Solvent	dn/dc (ml g^{-1})
Methanol	0,184	KOH M	0,158
Methanol+LiCl 0,4 M	0,180	KOH 0,1M/KCL 0,1M	0,166
Methylethylketone	0,153	NaOH 0,8M	0,160
Dimethylformamide	0,115	NaOH 0,01M/NaCl 0,1M	0,159

Table II reports the molecular weight data for some samples of unfractionated PLL which were prepared by interfacial polycondensation, in nearly similar experimental conditions.

Table II
Molecular weight data \bar{M}_w for unfractionated samples of PLL

Sample	$\bar{M}_w \cdot 10^{-5}$
PLL 5	2,8 (KOH 0,1M/KCL 0,1M)
	2,5 (NaOH 0,01M/NaCl 0,1M)
	2,3* (NaOH 0,01M/NaCl 0,1M)
PLL 6	2,2 (NaOH 0,01M/NaCl 0,1M)
	1,5* (Methanol)
	1,7* (Methanol+LiCl 0,4M)
	1,6 (Methylethylketone)
PLL 8	2,2 (NaOH 0,8M)
PLL 9	1,5* (NaOH 0,01M/NaCl 0,1M)

\bar{M}_w^* = according DEBYE method
others = according ZIMM method

As shown in this table, molecular weight calculated from DEBYE method are generally lower than those provided from ZIMM plots. For the PLL₆ sample, molecular weight value is found to be higher in aqueous medium than those obtained in organic medium; this result can be explained by the fact that refractive index increment measurements dn/dc in aqueous media were not carried out at constant chemical potential.

Anomalous ZIMM plots were observed for PLL solutions into methylalcohol and methylethylketone, therefore molecular weights in such solvents were determined by the DEBYE method.

From osmotic pressure experiments (18) for PLL₉ sample in aqueous media (NaOH 0,01M/NaCl 0,1M and NaOH 0,01M/NaCl 0,01M), the \bar{M}_n values were respectively $\bar{M}_n = 0.5 \cdot 10^5$ and $\bar{M}_n = 0.59 \cdot 10^5$. The corresponding polydispersity ratio \bar{M}_w/\bar{M}_n is then

$$\frac{\bar{M}_w}{\bar{M}_n} = 2,7$$

which is in rather good agreement with previously reported values for polysulfonamides (14). Otherwise \bar{M}_n could be estimated near of 10^5 from the angular dependence of scattered light (11).

FRACTIONATED SAMPLES

In the table III the characterization and Molecular weights of the fractionated sample are reported

Table III

Characterization of fractionated samples of PLL

Fraction No	I	II	III	IV	V
Weight (in g)	2,4	2,1	2,1	2,15	2,1
Monomeric unit (a)	349	347	352	356	359
$[\eta]_{350}^{25}$ (b)	330	339	339	351	330
$[\eta]$ dl g ⁻¹ (c)	0,23	0,30	0,33	0,35	0,46
$[\eta]$ dl g ⁻¹ (d)	0,54	0,61	0,80	0,86	1,01
$\bar{M}_w 10^{-5}$ (e)	1,03	1,30	1,47	1,57	1,93 (1)
	1,18	1,40	1,54	1,71	2,10 (2)

(a) determination by potentiometric titration (10) in non aqueous medium (th. = 348)

(b) molecular specific rotatory power ($\lambda=350\text{nm}$
C = 1% in methanol)

$$[\eta]_{350}^{25} = 345^\circ \text{ for unfractionated polymer}$$

(c) for PLL_E fractions in methylethylketone

(d) in KOH M

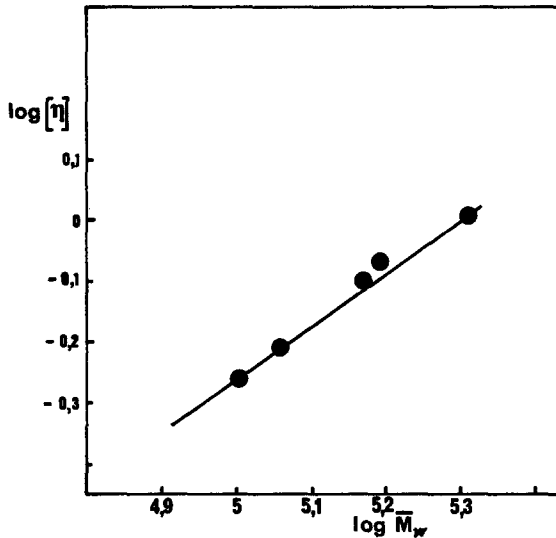
(e) \bar{M}_w in KOH M

(1) DEBYE method

(2) ZIMM method

A double logarithmic plot of intrinsic viscosity $[\eta]$ vs weight-average molecular weight \bar{M}_w for PLL in KOH 1M is shown in figure 1

Figure I



Double logarithmic plot of intrinsic viscosity

$[\eta]$ dl.g⁻¹ vs. weight-average mol.wt \bar{M}_w for PLL in KOH M

The following MARK-HOUWINK type relation was established in KOH 1M :

$$[\eta] \text{ dl.g}^{-1} = 2,7 \cdot 10^{-5} \bar{M}_w^{0,86}$$

The validity of the above intrinsic viscosity-molecular weight relationship was verified from recent low angle laser light scattering measurements performed with an other PLL sample : $[\eta] = 1,70 \text{ dl.g}^{-1}$ in KOH M.

\bar{M}_w measured = 367 000

\bar{M}_w calculated from viscosity = 380 000

Radii of gyration (R_G) and second virial coefficients (A_2) for PLL fraction I to V (in KOH 1M) were found in the range $R_G = 200\text{-}300 \text{ \AA}$ and $A_2 = 2\text{-}6 \cdot 10^{-4} \text{ ml.g}^{-2} \text{ mole.}$

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