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### Some Remarks on the Anionic Polymerization of Ethylene Oxide in Hexamethylphosphoramide

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LETTER TO THE EDITOR

## Some Remarks on the Anionic Polymerization of Ethylene Oxide in Hexamethylphosphoramide

A recent paper [1] on the anionic polymerization of ethylene oxide in hexamethylphosphoramide, using sodium and potassium as gegenions, shows that the living chains are associated. In the potassium case, the conductivity measurements were interpreted assuming formation of tetramers among ion pairs, which in turn ionize into free ions. The two dissociation constants for the tetramers to ion pairs and for the ion pairs to free ions were calculated. Viscosity measurements on the living and killed solutions confirmed the presence of aggregates, but no mention was made of the relation between the numerical values of both sets of measurements.

In this letter we try to throw some light on the complex behavior of this system. Assuming that the aggregated molecules in solution are of the star-shaped type, the theoretical ratios between the viscosities of living and deactivated polymers are calculated and the results are compared with the experimental ones.

The conductivity results have already been published [1]; let us recall the values obtained for the dissociation constants:  $3.0 \times 10^{-11}$  for the tetramer to ion pairs and  $4.6 \times 10^{-5}$  for the ion pairs to ions. The same applies to the viscosity results, except for one of them; in Table 1 we have specified the initiator concentration in mol/liter and the ratio  $(t_1 - t_0)/(t_k - t_0)$ , where  $t_1$  and  $t_k$  are the flow times for the living and deactivated polymer solutions, respectively, and  $t_0$  is the flow time for the solvent. The measurements were made in dilute solution and the polymers were a few thousands in molecular weight.

The tetramer must behave, hydrodynamically, as a branched molecule (a star with four branches of equal length). As known, branched molecules are more compact than linear ones of the same molecular weight. Because of this, the radius of gyration of the latter is larger than that of the former [2], and both are related by the "branching parameter,"  $g$ ,  $(\bar{s}^2_{\text{branched}}/\bar{s}^2_{\text{linear}}) = g$ . This parameter also relates the intrinsic viscosities of both polymers:  $([\eta]_{\text{branched}}/[\eta]_{\text{linear}}) = g^b$ . Unfortunately, there is no agreement on the value of the  $b$  exponent [2-4], although it seems to be experimental evidence that for star-shaped molecules, with three or four

equal branches in  $\theta$ -solvents (our case),  $b = 1/2$  [5, 6]. In nonideal solvents  $(1/2) < b < (3/2)$  [7]. Moreover, for this type of molecules,  $g^{1/2}$  is given by the expression [4]

$$g^{1/2} = \sqrt{\frac{3}{N} - \frac{2}{N^2}} \quad (1)$$

where  $N$  is the number of branches. In our case  $N = 4$  and  $g^{1/2} = 0.79$ .

The ratio  $([\eta]_{\text{living}}/[\eta]_{\text{killed}})$  can be calculated noting that  $[\eta]_{\text{living}} = [\eta]_{\text{branched}} \omega_{\text{branched}} + [\eta]_{\text{lineal}} \omega_{\text{lineal}}$ , where  $\omega_{\text{branched}}$  and  $\omega_{\text{lineal}}$  are the weight-fractions of the associated and nonassociated polymers, and  $[\eta]_{\text{branched}}$ ,  $[\eta]_{\text{lineal}}$  their respective intrinsic viscosities. Changing from weight to molar concentrations and recalling that, for star-shaped molecules, the factor  $g^b$  must be introduced in the Mark-Houwink-Sakurada equation, finally we get

$$\frac{[\eta]_{\text{living}}}{[\eta]_{\text{killed}}} = \frac{0.79 \times 8[\text{branched}] + [\text{lineal}]}{4[\text{branched}] + [\text{lineal}]} \quad (2)$$

where we have assumed  $\theta$  conditions and  $[\text{branched}]$  and  $[\text{lineal}]$  are the molar concentrations of associated and nonassociated species.

Since we know the dissociation constants of the tetramers and the ion pairs, it is possible to calculate  $[\text{branched}]$  and  $[\text{lineal}]$  for any initiator concentration, with  $[\text{lineal}] = [\text{ion pairs}] + [\text{free ions}]$ , and to evaluate a theoretical  $([\eta]_{\text{living}}/[\eta]_{\text{killed}})$ .

That relation also can be calculated, in an approximate way, from the flow times by

$$\frac{[\eta]_{\text{living}}}{[\eta]_{\text{killed}}} \approx \frac{t_1 - t_0}{t_k - t_0} \quad (3)$$

since we are working with dilute solutions and not very high molecular weights.

Table 1 shows the results for  $([\eta]_{\text{living}}/[\eta]_{\text{killed}})$  calculated from Eqs. (2) and (3). The first two values are in satisfactory agreement, and they confirm the formation of tetramers from ion pairs in accordance with the high tendency of the ethylene oxide alkoxides to aggregate [8] and in spite of the moderately high dielectric constant of the solvent. The discrepancy in the last value may arise from destruction of living species or, since this is the most concentrated of the three solutions, from the inadequacy of Eq. (3) when used with finite concentrations. It is remarkable that with such different experimental techniques as viscometry and conductimetry the same conclusions can be obtained.

**Table 1.**  $[\eta]$  living/ $[\eta]$  killed from Viscosity Measurements and Conductivity Results

Run	$10^4[\text{KOR}]$	$\frac{[\eta]_{\text{living}}}{[\eta]_{\text{killed}}} = \frac{t_1 - t_0}{t_k - t_0}$	$\frac{[\eta]_{\text{living}}}{[\eta]_{\text{killed}}}$ from Eq. (2)
VHA <sup>a</sup>	2.14	1.07	1.07
VHB	20.7	1.41	1.44
VHC	57.9	1.21	1.58

<sup>a</sup>Unpublished result.

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