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LETTER TO THE EDITOR

Association: A Possible Explanation for Anomalies in Ebulliometric Measurements with Polyethylene

In a recent paper [1], anomalies in ebulliometric measurements with polyethylene in different solvents were reported. Anomalies were claimed because the elevation of the boiling point ΔT exhibited an unusual concentration dependence. A strong increase of ΔT with c was followed by a weaker one and again by a strong increase. The anomalies at low concentrations were attributed to unaccounted-for factors.

This unaccounted-for factor may, however, well be association. The arguments in favor of this explanation are as follows. Replotting the data as reduced boiling point elevation $\Delta T/c$ as a function of concentration c gave curves with a minimum and a nonlinear behavior at low concentrations. Such curves are characteristic for associating solutes in good solvents, if the association is a consecutive process (open association: $2M_I \rightleftharpoons M_{II}$, $M_{II} + M_I \rightleftharpoons M_{III}$, $M_{III} + M_I \rightleftharpoons M_{IV}, \ldots$) [2]. Open association in good solvents has been shown to occur with polyurea [3], poly(ethylene oxides [4], and polypropylenes [5] by light scattering [3] and vapor-pressure osmometry [4, 5].

In the theta state, a linearization of the data is possible which may be used as a check for the presence of association. Assuming an independence of the equilibrium constant of open association ${}^{n}K_0$ on particle weight, one arrives at [6].

$$(M_n)_{app,\theta} = (M_I)_n + 10^3({}^{n}K_0)(M_I)_n(c/(M_n)_{app,\theta} \tag{1}$$

where $(M_n)_{app,\theta}$ is the apparent number-average molecular weight in the theta state and $(M_I)_n$ the true number-average molecular weight in the nonassociated state (molecular weight of the unimer). For small ${}^{n}K_0$, Eq. (1) reduces to [4, 6]

$$(M_n)_{app,\theta} = (M_I)_n + 10^3({}^{n}K_0)c \tag{2}$$

For arbitrary solvents, the apparent molecular weight in the theta state may be related to the apparent molecular weight by

$$1/(M_n)_{app} = (1/M_n)_{app,\theta}) + \frac{\sum_i (A_2)_i c_i^2}{\mathcal{R}Tc} \qquad (3)$$

In this derivation, the second virial coefficients $(A_2)_i$ of the i species were assumed to contain besides polymer–solvent interactions, etc., the *intra*molecular polymer–polymer interaction only, whereas the *inter*molecular polymer–polymer interactions ("chemical interactions") are included in the first right-hand term of Eq. (1).

In Fig. 1 the apparent number-average molecular weights $(M_n)_{app}$ are plotted against the concentration c according to Eq. (2). A very good linear relationship between these two quantities is obtained at concentrations below ca. 0.02 g/ml. The deviations at higher concentrations are due to positive 2nd virial coefficients A_2 as suggested in [1].

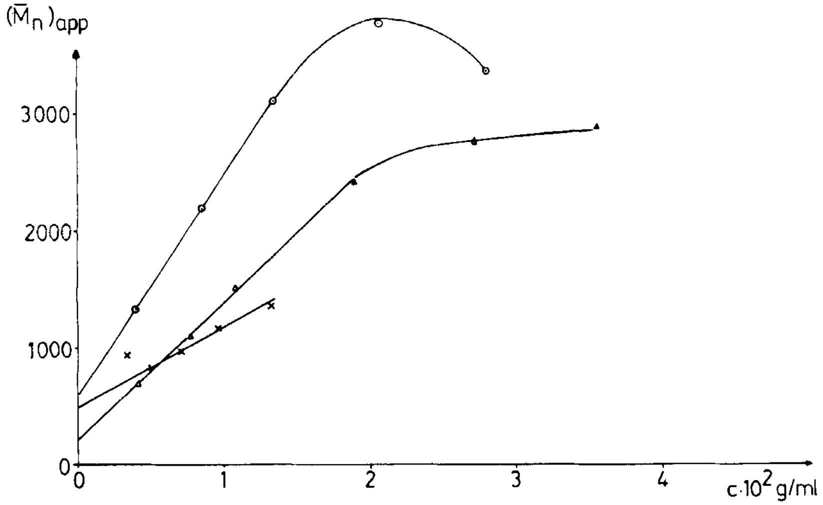

FIG. 1. Concentration dependence of the apparent number-average molecular weights of polyethylenes. ⊙ Marlex 6009 in p-xylene; x, △ Ziegler polyethylenes in bromobenzene.

The equilibrium constants of association (Table 1) are relatively low compared with those of the polypropylenes [5]. The number-average molecular weights are very low, which may be due to a tailing of the molecular weight distribution curve or impurities. Broad distributions are familiar with high-density polyethylene.

TABLE 1. Number-Average Molecular Weights $(M_I)_n$ and Association Constants $^nK_0$ of Polyethylenes

Sample	Solvent	Molecular weight $(M_I)_n$, g/mole	Association constant $^nK_0$, liter/mole
Marlex 6009 (⊙)	p-Xylene	580	190
Ziegler I (x)	Bromobenzene	480	70
Ziegler II (△)	Bromobenzene	200	120

A more rigorous check on association would naturally be by changing the solvent, the temperature, and the method (e.g., vapor-pressure osmometry). However, no data are given in the cited paper [1].

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