

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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

Hans-Georg Elias

To cite this Article Elias, Hans-Georg(1968) 'Association: A Possible Explanation for Anomalies in Ebulliometric Measurements with Polyethylene', *Journal of Macromolecular Science, Part A*, 2: 1, 215 – 217

To link to this Article: DOI: 10.1080/00222336808053359

URL: <http://dx.doi.org/10.1080/00222336808053359>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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 non-linear behavior at low concentrations. Such curves are characteristic for associating solutes in good solvents, if the association is a consecutive process (open association: $2M_I \rightleftharpoons M_{II}$, $M_{II} + M_I \rightleftharpoons M_{III}$, $M_{III} + M_I \rightleftharpoons M_{IV}$, ...) [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 nK_0 on particle weight, one arrives at [6].

$$(M_n)_{\text{app}, \theta} = (M_I)_n + 10^3({}^nK_0)(M_I)_n(c/(M_n)_{\text{app}, \theta}) \quad (1)$$

where $(M_n)_{\text{app}, \theta}$ 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 nK_0 , Eq. (1) reduces to [4, 6]

$$(M_n)_{\text{app}, \theta} = (M_I)_n + 10^3({}^nK_0)c \quad (2)$$

For arbitrary solvents, the apparent molecular weight in the theta

state may be related to the apparent molecular weight by

$$1/(\bar{M}_n)_{app} = (1/\bar{M}_n)_{app,\theta} + \frac{\sum_i (A_2)_i c_i^2}{R T c} \quad (3)$$

In this derivation, the second virial coefficients $(A_2)_i$ of the i species were assumed to contain besides polymer-solvent interactions, etc., the *intramolecular* polymer-polymer interaction only, whereas the *intermolecular* 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 $(\bar{M}_n)_{app}$

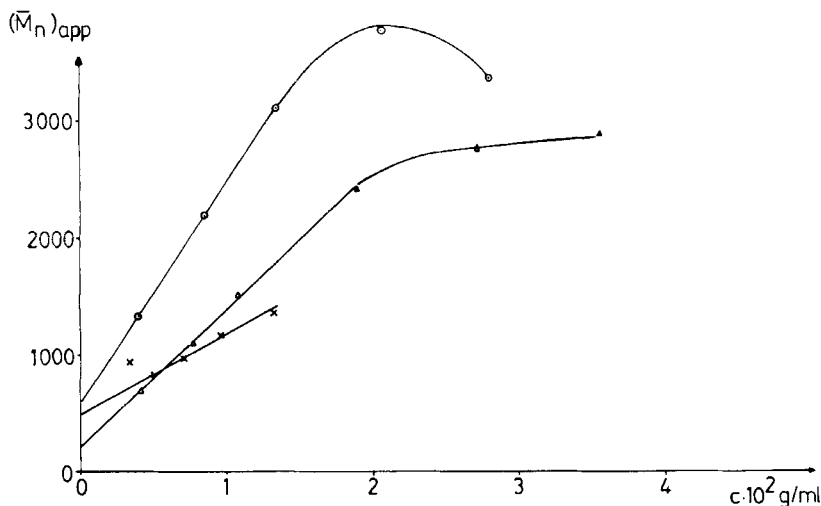


FIG. 1. Concentration dependence of the apparent number-average molecular weights of polyethylenes. \odot Marlex 6009 in p-xylene; \times , Δ Ziegler polyethylenes in bromobenzene.

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].

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 $(M_p)_n$ and Association Constants nK_0 of Polyethylenes

Sample	Solvent	Molecular weight $(M_p)_n$, g/mole	Association constant nK_0 , liter/mole
Marlex 6009 (⊙)	p-Xylene	580	190
Ziegler I (x)	Bromobenzene	480	70
Ziegler II (Δ)	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].

Acknowledgment

I would like to thank Dr. G. R. Williamson for supplying me with the original ebulliometric data.

REFERENCES

- [1] G. R. Williamson, *J. Polymer Sci.*, **A2(5)**, 394 (1967).
- [2] H.-G. Elias, *Helv. Chim. Acta*, **48**, 1018 (1965).
- [3] J. Feisst and H.-G. Elias, *Makromol. Chem.*, **82**, 78 (1965).
- [4] H.-G. Elias and H. Lys, *Makromol. Chem.*, **96**, 64 (1966).
- [5] H.-G. Elias and H. Dietschy, *Makromol. Chem.*, **105**, 102 (1967).
- [6] H.-G. Elias and R. Bareiss, *Chimia (Aarau)*, **21**, 53 (1967).

Hans-Georg Elias

*Department of Industrial and Engineering Chemistry
Swiss Federal Institute of Technology
Zurich, Switzerland*

*Accepted by editor November 29, 1967
Submitted for publication January 2, 1968*