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Short Communication

The influence of molecule-size on the state of order and on the order-dependent properties of ointments*

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Some years ago we observed that the consistency and the liquid-immobilization of ointments increased according to the logarithm of the molecular weight in the solid phase (Hüttenrauch et al., 1972, 1973). Later on it was found independently that these properties correlated with the degree of order in the solid phase (Hüttenrauch and Fricke, 1979). Therefore, we now suggest a relationship between both results.

In the event that a logarithmic correlation could be proved between molecular weight and degree of order as between molecular weight and ointment properties, the influence of molecule-size upon the dosage form could be interpreted as an influence of the state of order. We therefore examined the problem using, as examples, hydrocarbon ointments.

As is well known, the degree of order decreases (and the degree of disorder increases) within most of the homolog polymer series corresponding to the enlargement of the molecules (Wolf, 1962). Among paraffins and polyethylenes, the influence of molecular weight on crystallinity has been studied several times. However, the reported results and the derived laws do not agree with each other. In particular there are anomalies in the regions up to molecular weight 2000 and above molecular weight 12,000. Low-molecular compounds show an increase in crystallinity in accordance with the increase of molecule-size (Matthews et al., 1949; Überreiter et al., 1952). Among high-molecular compounds a constant final value (Matthews et al., 1949) or a continuous decrease of imperfections (Tung and Buckser, 1958) was established. Consequently, in the graph relating the molecular weight with the degree of order an extreme value can be seen (Matthews et al., 1949). A similar shape of the curve results by plotting the dependence between the chain length and the distance of crystallites (respectively the breadth of disordered zones) or between the molecular weight, the velocity of crystallization and the disarrangement (Überreiter and Orthman, 1952).

Initially, we evaluated the law of the X-ray-metric measurements published by Matthews et al. (1949). A logarithmic dependence between molecule-size and degree of order was recognized (regarding the range between molecular weight 2000 and 12,000) (Fig. 1). We also found a logarithmic relation evaluating dilatometric data (Tung and Buckser,

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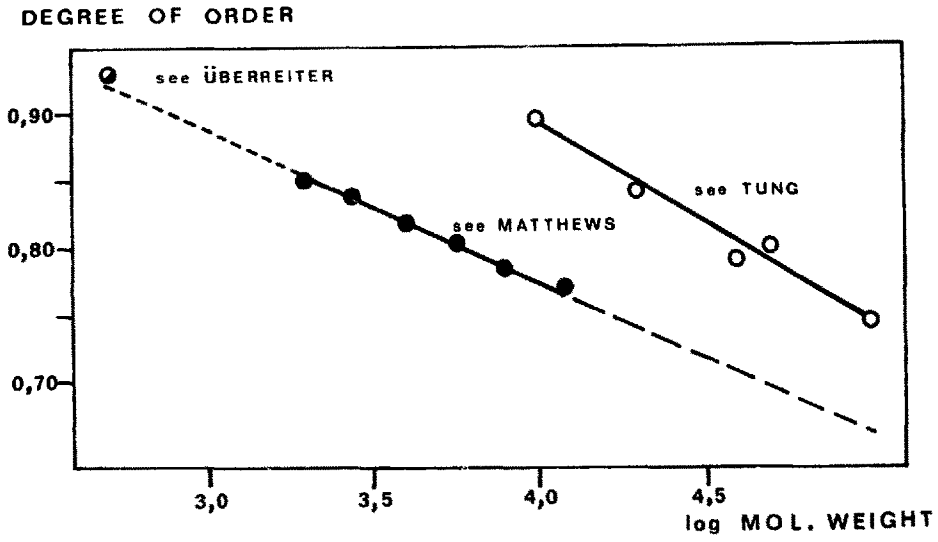

Fig. 1.

1958). The measurements concern high-polymer polyethylenes. In the semi-logarithmic diagram linearity was established (Fig. 1), the two curves being almost parallel.

Therefore the line obtained from X-ray-metric data was extrapolated up to the molecular weight 100,000. The extrapolation in the other direction up to the molecular weight 500 resulted surprisingly in an order-value, which was also found experimentally (Überreiter and Orthman, 1952). As to solid paraffin, we found graphically a crystallinity of 92.5% while the volumetrically analyzed value amounted to 93.0%. Therefore, the state of order alters over a wide range in dependence on the logarithm of the molecular weight (Fig. 1).

In preparing model ointments, 3 solid hydrocarbons were used, which differed considerably in their molecular weight. These compounds possessed, with respect to the described logarithmic relation, the following characteristics (Table 1).

15% of the solids and 85% of the liquid paraffin each were combined. In the prepared ointments the penetration value and the bleeding value were determined (Hüttenrauch et al., 1972).

TABLE 1

	Molecular weight (viscosimetric)	C-number, degree of polymerization	Chain length (unbranched, theoretical)	Degree of order
Solid paraffin	524.8	37	4.54 nm	0.925
Polyethylene wax	4786.3	342	42.97 nm	0.810
Polyethylene	61,659.5	4404	554.78 nm	0.683

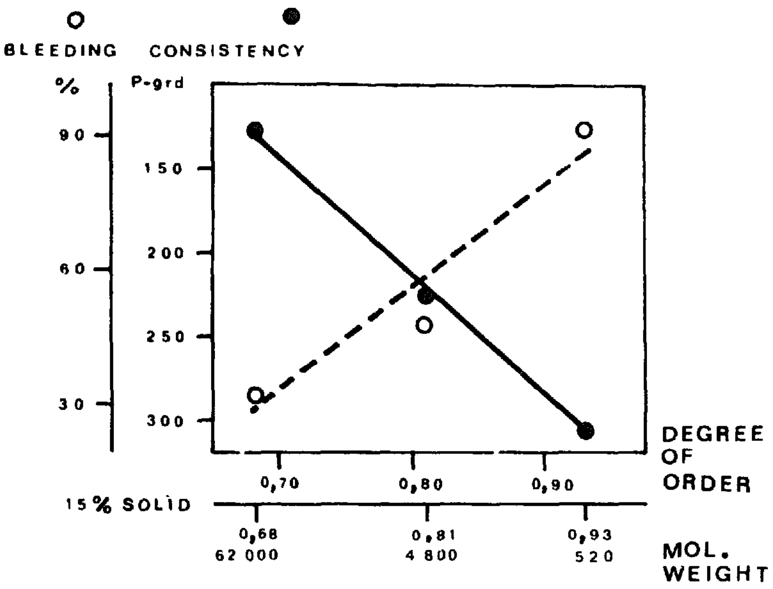

Fig. 2.

Correlating the measurements with the described degree of order in the solid phase produced the curve illustrated in Fig. 2.

Firstly the properties of the ointments and secondly, the degree of order is in logarithmic relation to the molecular weight. Therefore, a linearity exists between the behaviour and the state of order. The influence of molecule-size on the ointment properties and the logarithmic validity of this influence are thus highly probably caused by the relation between chain length and degree of disorder.

This result again confirms the importance of lattice imperfections in forming the gel-like properties of ointments.

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