

LETTERS TO THE EDITORS

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A New Method of fractionating High Polymers

WE wish to report the results of some exploratory experiments which have been attempted in order to establish a new method for fractionating high polymers.

Zone melting is now recognized as a method of producing materials having a very high degree of purity<sup>1</sup>. Used in the conventional manner, it is found that some impurities are more readily eliminated than others. If, in the case of a high polymer added to a solvent having a suitable melting point, the polymer is eliminated upon zone melting by a process dependent upon some physical parameter which is a function of the degree of polymerization, then this could be used as the basis of a means of fractionation.

In one experiment, a glass tube closed at the base, of 2.2 cm. internal diameter and 30 cm. length, was filled with molten naphthalene. This was first purified by raising the column slowly through a close-fitting heater supplied from a variable voltage source, and the voltage adjusted to give as narrow a molten zone as possible. There was considerable degassing during this process and also purification of the naphthalene, as evidenced by the decreasing opacity of the column after each pass through the heater. After eight passes there was little further change in the purity of the naphthalene contained in the upper portions of the tube.

200 mgm. of polystyrene (D.C.P.J.3, Distillers Co., Ltd., Epsom, Surrey.  $\bar{M}_n = 80,000$ ,  $\bar{M}_w = 200,000$ ) was put on the top of the column and taken into solution by arranging the heater and adjusting the heater voltage so that the upper 6 cm. was held in a molten state for 6 hr. This means that initially the polymer was present at 1 per cent concentration at the top of the column. A pronounced opacity, in a region which was formerly transparent, clearly indicated the position of the polymer when the naphthalene solidified. Zone melting was then carried out, using a rate of passage through the heater of 1 in./hr. After one pass it was estimated visually that the polymer had moved 3 cm. down the column, and so was dispersed

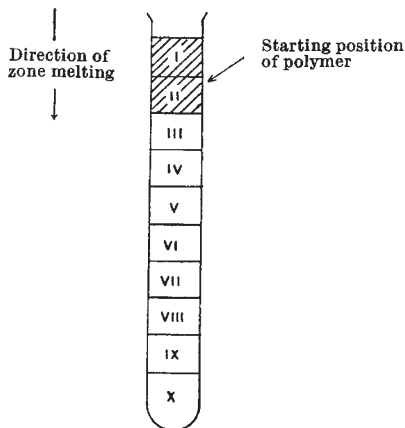


Fig. 1. The column used, showing the initial position of the polystyrene and of fractions recovered

Fraction	I	II	III	IV	V	VI	VII	VIII	IX	X
Weight of polystyrene (mgm.)	8.0	7.0	7.5	8.1	6.8	6.4	7.2	6.2	4.6	10.6

throughout the upper 9 cm. Eight passes were sufficient to distribute the polymer throughout the whole of the column.

The polymer was recovered by cutting out the polymer-naphthalene mixture with a flat-faced wood drill so as to produce ten approximately equal portions, and subliming away the naphthalene, which left the polymer in a very fine fibrous state.

The weights of the polymer recovered are given in Table 1, and the positions of the fractions on the column shown in Fig. 1.

The molecular weight and molecular weight distribution of each fraction were assessed qualitatively by turbidimetric titration<sup>2</sup>. In each case 35 ml. of the polystyrene solution, containing 4 mgm./100 ml., was placed in the titration cell, together with 10 ml. of dried methanol. The change in transmission of a light-beam passing through the cell was measured at 1-min. intervals while a further 10 ml. of methanol was added continuously at the constant rate of 0.135 ml./min.

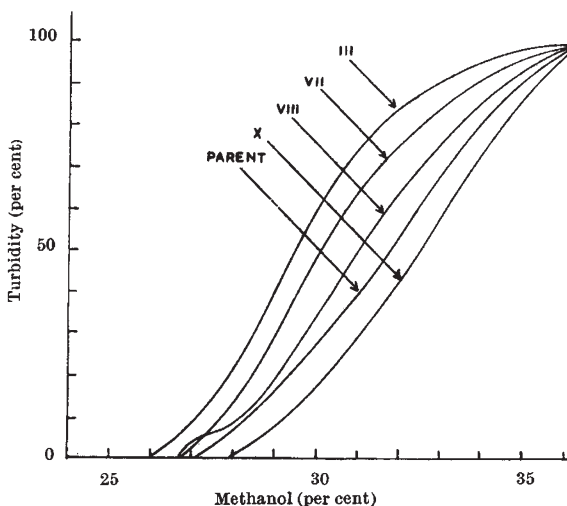


Fig. 2. Turbidimetric titration of the parent polymer and the polystyrene fractions in benzene solution using methanol as precipitant

Fig. 2 shows the change in turbidity of the cell contents with the addition of methanol. The parent material is precipitated over a wide range of solvent-non-solvent ratios, and the materials recovered from the column after zone refining show a much narrower range of precipitation; also the initial precipitation points move in a well-defined sequence.

From this experimental evidence, it can be concluded that the zone melting process can be applied to the fractionation of high polymers. Further investigation of the method is in progress.

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<sup>1</sup> Parr, N. L., "Zone Refining", Royal Institute of Chemistry Monograph (1957).  
<sup>2</sup> Melville, H. W., and Stead, B. D., *J. Polymer Sci.*, **16**, 505 (1955).