# *The Anomalous Osmotic Behaviour of Polymethacrylonitrile.*

By N. GRASSIE and E. VANCE.

**[Reprint Order No. 5072.]**

Reliable determinations of the number-average molecular weight of polymethacrylonitrile are not possible from osmotic-pressure measurements in ethyl methyl ketone solution. With this solvent, S-shaped $\pi/c$ against $c$ curves are obtained which cannot be satisfactorily extrapolated to zero concentration. The shape of these curves, the effect of temperature, and the peculiar solution properties of this system have been explained qualitatively in terms of competing polymer–solvent and polymer–polymer association.

*cyclo*Hexanone and acetone are the only two solvents in which polymethacrylonitrile exhibits normal osmotic and solution behaviour. Of these, the former has been found to be entirely satisfactory for the osmotic determination of molecular weights.

IN the general investigation of polymeric reactions, and particularly in kinetic work in this field, it is usually convenient to be able to measure number-average molecular weights which may be most readily deduced from osmotic pressure measurements. On plotting $\pi/c$ against $c$ (where $\pi$ is the osmotic pressure of a solution of concentration $c$) non-ideal behaviour is invariably encountered, most polymer–solvent systems, however, being fairly well represented either by the linear expression $\pi/c = P + Qc$ or by $\pi/c = P + Qc + Rc^2$, which have been given ample theoretical justification by Huggins (*Ind. Eng. Chem.*, 1943, **35**, 216, 980). At all events, the linear or gently curved plots are usually fairly easily extrapolated to zero concentration, the intercept on the $\pi/c$ axis, $(\pi/c)_0$ (= $P$), being used to calculate the molecular weight of the solute from the classical equation $(\pi/c)_0 = \boldsymbol{R}T/M$.

The number of solvents for polymethacrylonitrile is restricted, the interaction between chains which causes the almost complete insolubility of polyacrylonitrile being only slightly eased by the introduction of the methyl group. Polymethacrylonitrile swells in chloroform, is soluble in cold solutions of methylene chloride and ethyl methyl ketone, and is freely soluble only in acetone and *cyclo*hexanone. Of these last four solvents methylene chloride and acetone present certain difficulties in osmotic work owing to their volatility. Ethyl methyl ketone and *cyclo*hexanone therefore appeared to be most suitable for routine measurements.

In ethyl methyl ketone at 23°, polymer A ($M = 63{,}000 \pm 2{,}000$, see p. 2125) is found to give the completely novel type of curve shown in Fig. 1 (curve 1). This curve can be delineated accurately and reproducibly on a much wider vertical scale than that shown, so that there can be no doubt about the principal details of its shape. Also on Fig. 1 (curves 2 and 3) can be seen the marked changes which take place in the shape of the osmotic pressure curves with temperature. It is quite clear then that at the most convenient temperatures for osmotic pressure measurement (20—30°) an accurate extrapolation to zero concentration would be impossible, while even at 4° the fact that the slope is increasing with decreasing concentration at low concentrations would make the value of any extrapolation extremely doubtful.

Also in Fig. 1 are curves (4 and 5) obtained with solutions in *cyclo*hexanone, which exhibit normal behaviour, the slopes increasing with temperature but giving intercepts identical within experimental error. This intercept is obviously a reasonable one for the ethyl methyl ketone curves at 4° and 23°, and it must be assumed that at some lower concentration the 30° curve bends upwards also towards this ultimate value, which represents a molecular weight of 63,000 ± 2,000. Fig. 2 includes a similar series of curves derived from measurements made on polymer B ($M$ = 137,000 ± 5,000; see p. 2125).

FIG. 1. Osmotic curves for Polymer A ($M$ = 63,000 ± 2,000) in ethyl methyl ketone (1, 23°; 2, 4°; 3, 30°) and in *cyclo*hexanone (4, 30°; 5, 35°).

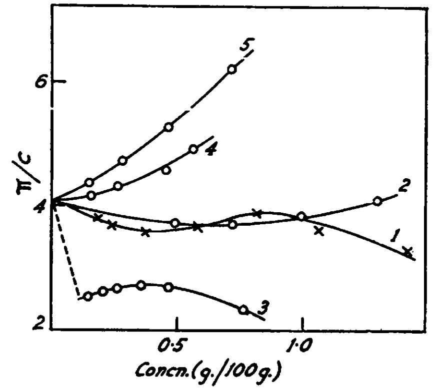
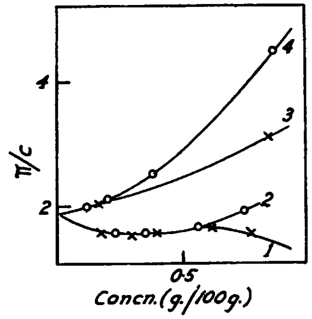


FIG. 2. Osmotic curves for Polymer B ($M$ = 137,000 ± 5,000) in ethyl methyl ketone (1, 24·5°; 2, 4°) and in *cyclo*hexanone (3, 25°; 4, 35°).



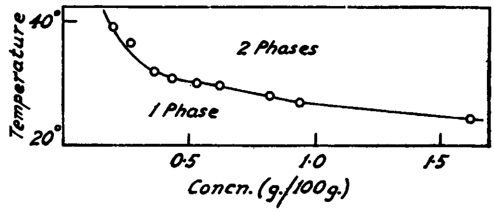


FIG. 3. Solubility of Polymer A in ethyl methyl ketone.

An interesting property of the ethyl methyl ketone–polymethacrylonitrile system, and one which is clearly associated with its anomalous osmotic behaviour, is the fact that solubility increases with decreasing temperature. A 1% solution prepared at 4° becomes quite cloudy at 28° but remains crystal clear at −78°; it may be significant that ethyl methyl ketone is one of those substances which give a completely closed mutual solubility curve with water (Rothmund, *Z. physikal. Chem.*, 1898, **26**, 433).

The solution properties of polymers make it difficult to obtain accurate solubility curves by conventional methods. Precipitation in such systems takes place by the gradual aggregation of molecules over a fairly wide temperature range. Some arbitrary definition of precipitation must therefore be made for convenience, and the simplest in the present case is concerned with the visual appearance of cloudiness. Fig. 3 records a solubility curve obtained by slowly warming and cooling solutions of polymer A and plotting the average of the temperatures at which cloudiness appears and disappears in each case. These pairs of temperatures were always within 1—2° of each other. When cloudiness appears the molecular aggregates must have become quite large and it is to be expected that the osmotic pressure of the system should be falling fairly rapidly with increasing concentration. There is at least qualitative agreement in this respect between the data in Fig. 3 and the ultimate decrease in $\pi/c$ at high concentration shown by the ethyl methyl ketone curves in Fig. 1. Even at the lowest concentrations, however, the beginnings of precipitation are discernible from the decreasing values of $\pi/c$ with increasing concentration, although the reason for the inflexions in the curves between these two extremes of concentration requires further consideration.

The amount of aggregation, or the number of aggregative interactions between molecules, obviously increases with concentration so that we may write $\alpha = \mathrm{f}(c)$, where $\alpha$ is the number of aggregative interactions between different molecules per mole of polymer, and $\mathrm{f}(c)$ is some function of concentration which increases with concentration. It follows that $\mathrm{C.L.} = \mathrm{C.L.}_0/(1 - \alpha) = \mathrm{C.L.}_0/[1 - \mathrm{f}(c)]$ where C.L. and $\mathrm{C.L.}_0$ are the average numbers of monomer units in molecular aggregates and single molecules respectively, *i.e.*, at concentrations $c$ and zero. As the concentration increases from zero, the effect of this function is to give a negative slope to the curve of $\pi/c$ against $c$. With increasing concentration, however, at low concentrations this negative slope increases only slightly and is soon overtaken by the rapidly increasing positive slope due to the terms $Qc$ and $Rc^2$ resulting in a point of inflexion followed by a positive slope. As $\mathrm{f}(c)$ approaches unity $\mathrm{C.L.}_0/[1 - \mathrm{f}(c)]$ rapidly approaches an infinitely high value, resulting in another point of inflexion and a rapid decrease in $\pi/c$, ultimately to zero.

The effect of temperature on the ethyl methyl ketone curves is explicable in the same terms as the increasing solubility with decreasing temperature. Substances which are not composed of giant or highly cross-linked molecules are freely soluble or insoluble respectively according as solute–solvent or solute–solute interaction predominates. In this system, in which both solvent and solute are relatively highly polar, polymer–polymer and polymer–solvent interactions are fairly strong and apparently also finely balanced. At lower temperatures polymer–solvent interaction predominates. Thus polymer–polymer interaction tends to be suppressed, agglomeration is largely prevented, and the osmotic curves approach normality. As the temperature is raised, polymer–solvent association is broken down progressively, allowing the less mobile polymer molecules to interact. Thus, although the effect of temperature increase will also be to make polymer–polymer interactions weaker, it also enables interaction between individual molecules at an increasing number of points by reason of the progressive removal of solvent from the environment of polymer molecules. In the range of temperatures studied, the latter process evidently prevails, giving the solubility and osmotic characteristics reported above.

While S-shaped osmotic curves of this type have not previously been reported, negatively sloping curves or parts of curves have been observed in a few instances and in each case have been explained by molecular association; *e.g.*, Steurer (*Z. physikal. Chem.*, 1942, **190**, 1) found that the osmotic pressure curves for ethyl cellulose in benzene and toluene are normal positively sloping straight lines down to concentrations of about 0·1—0·2%, below which they curve steeply upwards to very much higher values of $\pi/c$. The ultimate value at zero concentration is believed, although not proved, to be the same as that obtained when using solvents giving normal curves, so that, as in the present work, association appears to exist in the form of a dynamic equilibrium. By contrast with this, Doty (*J. Amer. Chem. Soc.*, 1947, **69**, 1631) has had to postulate a static association of polyvinyl chloride molecules in dioxan. In this case, the slope of the linear osmotic pressure curves decreases with temperature until at 14° a negative slope is obtained. Instead of giving a constant intercept on the $\pi/c$ axis, however, $(\pi/c)_0$ decreases with decreasing temperature. Hence, even at the lowest concentrations association shows no signs of breaking down.

## EXPERIMENTAL

Methacrylonitrile was prepared by acetylation of acetone cyanohydrin followed by pyrolysis of the resulting acetate. Acetone cyanohydrin (1 mol.) and acetic anhydride (1·5 mol.) were allowed to react at room temperature for 24 hr. Distillation of the resulting mixture gave an acetone cyanohydrin acetate fraction (b. p. 180—185°). This was passed dropwise into a vertical silica tube about 4′ long and 3″ in diameter, which was packed with silica chips and heated electrically to 550°. The mixture collected at the bottom was poured into water, and the monomer extracted with ether, the ether extract being washed with water and dried ($Na_2SO_4$). The ether was removed by distillation, and the fraction of methacrylonitrile distilling between 92° and 94° collected (yield, 70% on acetone cyanohydrin).

Polymers A and B were obtained by polymerising the above monomer *in vacuo,* after degassing and twice distilling it *in vacuo,* at 80° and 70°, respectively, and in presence of 0·2% of benzoyl peroxide as catalyst. Polymerisation was continued to approx. 15% conversion. The polymer was isolated by dissolving this mixture in acetone, pouring the solution into methyl alcohol–water (75 : 25), and drying the resulting powder at 80° in air.

Osmotic pressure measurements were made on a Fuoss–Mead type instrument as modified by Masson and Melville (*J. Polymer Sci.*, 1949, **4**, 323), bacterial cellulose membranes being used.

We thank Imperial Chemical Industries Limited, Billingham, for supplies of acetone cyanohydrin and details of the preparation of methacrylonitrile from it, made available through Dr. Coates. We also thank the D.S.I.R. for the award of a Maintenance Allowance (E. V.), and the University of Glasgow for the award of an I.C.I. Research Fellowship (N. G.), during the tenures of which this work was carried out.

THE UNIVERSITY, GLASGOW, W.2.

[*Received, January 28th,* 1954.]