

# Viscosity—molecular weight relationship for cellulose tripropionate in chloroform

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The hitherto unreported constants in the Mark—Houwink viscosity—molecular weight relationship have been determined for both number-average and weight-average molecular weights for cellulose tripropionate in chloroform. Five narrow molecular weight range samples of a prepared cellulose tripropionate were obtained by fractional precipitation and characterized by osmometric and g.p.c. measurements. The cellulose tripropionate chain showed a high rigidity, characteristic of cellulosic polymers, but appeared to be more flexible than the corresponding triacetate in the same solvent.

## INTRODUCTION

A recent survey<sup>1</sup> of viscosity—molecular weight Mark—Houwink constants for cellulose esters, while including data for the acetate, butyrate and nitrate, makes no reference to cellulose propionate. A subsequent literature search has, in fact, showed the absence of any published work on the viscosity—molecular weight relationship for cellulose propionate.

The present work was carried out to determine the constants in the Mark—Houwink viscosity—molecular weight equations for both the number-average molecular weight ( $\bar{M}_n$ ) and weight-average molecular weight ( $\bar{M}_w$ ) using fractionated samples of cellulose tripropionate. Care was taken to make measurements over a sufficiently wide range of molecular weights (5.4:1) with fractions having low  $\bar{M}_w/\bar{M}_n$  ratios (<1.32). These conditions satisfy the accepted criteria for reliable values of  $K$  and  $a$  when the viscosity-average molecular weight ( $\bar{M}_v$ ) is replaced by either  $\bar{M}_n$  or  $\bar{M}_w$  in the expression  $[\eta] = K(\bar{M}_v)^a$ , where  $[\eta]$  is the limiting viscosity number ( $LVN$ ) for the solution.

## EXPERIMENTAL

### Materials

Cellulose tripropionate (CTP) was prepared from purified cotton linters (supplied by Holden Vale Manufacturing Co. Ltd, Lancs.) using a propionic acid—propionic anhydride—carbon disulphide mixture with zinc chloride as catalyst at 40°C. The product was analysed by a modified saponification method<sup>2</sup> to give a propionic acid content of 67.10% (theoretical 67.28%) and had an  $\bar{M}_n$  value of  $2.31 \times 10^5$ . Laboratory grade acetone and propionic acid, and Analar grade petroleum spirit (b.p. 60°–80°C) were used in the fractionation procedure. Analar chloroform and tetrahydrofuran (free of stabilizer) were used for the viscometric, osmometric, and gel permeation chromatography (g.p.c.) measurements.

### Fractionation of CTP

Fractionation was carried out using two different solvent—non-solvent systems which were being investigated. In the first, a 2 l solution of CTP in acetone ( $10 \text{ g l}^{-1}$ ) was prepared and aged for two days at 20°C before fractionation. Petroleum spirit was added to the solution, with stirring, until it became distinctly turbid. The turbidity was cleared by warming and the precipitated CTP allowed to form again by slowly cooling the solution to 20°C with stirring. The warming and cooling procedure was again repeated and the solution finally left to stand overnight at 20°C. The precipitated CTP fraction was then easily separated from the clear solution by decantation, redissolved in acetone, precipitated again with excess petroleum spirit and finally dried in a vacuum oven at 60°C. Subsequent fractions were obtained in the same way by further addition of precipitant to the decanted solution.

In the second system water was added as precipitant to a 1 l solution of CTP in propionic acid ( $9.8 \text{ g l}^{-1}$ ) at 20°C. After the warming and cooling step it was necessary to separate the precipitated CTP by centrifugation. After decantation the precipitate was dissolved in acetone, reprecipitated with water and dried as before. Only one CTP fraction prepared in this way was subsequently used in the viscosity—molecular weight studies.

### Viscometry

Chloroform stock solutions were prepared from CTP samples dried in a vacuum oven at 110°C, and then aged for 2–3 days at 25°C before use. Solution flow-times were measured in an Ubbelohde viscometer at 25°C using a stopwatch reading to 0.01 secs. Liquids entering the viscometer were prefiltered (Sinter No. 3) and solvent evaporation and moisture contamination minimized by attached solvent traps and drying tubes. Different polymer concentrations were obtained by solvent dilution of stock solution in the viscometer, mixing being effected by a stream of dry air saturated with solvent at 25°C. Flow times recorded were the mean of three consecutive readings agreeing to within  $\pm 0.05$  sec in each case.

Table 1 Molecular weights and limiting viscosity numbers for CTP fractions in chloroform at 25°C

Fraction	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$	LVN (dlg <sup>-1</sup> )
1	389 200	1.32	513 700	3.720
2	270 000	1.30	351 000	2.644
3	197 300	1.27	250 600	1.948
4	153 100	1.17	179 100	1.483
5	72 000	1.15	82 800	0.7471

Values of LVN for each fraction were obtained by least squares treatment of the viscosity number *versus* concentration plots in the usual way. A suitable degree of polynomial equation to best describe each set of data was employed for the least squares method. Kinetic energy and shear gradient effects were considered to be negligible and corrections for these were not applied to viscosity data. Plots contained 5–10 sets of data within an overall concentration range of 0.03–1.0 g dl<sup>-1</sup>.

#### Osmometry

$\bar{M}_n$  values were obtained using a Hewlett–Packard Mechrolab Model 502 membrane osmometer at 25°C, with a Schleicher–Schuell gel Cellophane membrane (type 0–8) which had been carefully conditioned to the solvent. The different CTP concentrations in chloroform were made up separately under the same conditions for the viscometry stock solutions. Equilibrium osmotic heads remained constant to ±0.01 cm and a preliminary  $\bar{M}_n$  determination using a standard molecular weight polystyrene polymer (Waters Associates Ltd  $\bar{M}_n = 96\ 200$ ) showed agreement to within 1%. Values of  $\bar{M}_n$  for CTP fractions were obtained by least squares treatment of the linear plots of reduced osmotic head *versus* concentration in the usual way. Plots contained five sets of data (fraction 2 contained four) within an overall concentration range of 0.1–1.6 g dl<sup>-1</sup>.

#### Gel permeation chromatography

G.p.c. measurements were used to check the molecular weight heterogeneity of each CTP fraction as defined by its  $\bar{M}_w/\bar{M}_n$  value. These ratios were then combined with osmometric  $\bar{M}_n$  values to evaluate weight-average molecular weights for CTP. This procedure was considered to give the more reliable  $\bar{M}_w$  data, in view of the uncertainties inherent in g.p.c. calibration methods and the fact that  $\bar{M}_n$  values are based on an absolute method.

A Waters Associates Ltd Model 200 apparatus, incorporating a FICA MK I Viscomatic automatic viscometer (at 30°C) was employed. Runs were made in degassed tetrahydrofuran with Styragel columns at room temperature. CTP samples were vacuum oven dried at 95°C and solutions made up in a dry-box to avoid moisture contamination. Solutions were aged for at least 24 h under nitrogen before injection into the g.p.c. apparatus. Calibration was carried out using standard narrow molecular weight distribution samples of polystyrene (Waters Associates Ltd) based on hydrodynamic volume considerations. A preliminary study showed this to be a better approach for CTP than the 'Q-factor' calibration method<sup>3</sup>.

## RESULTS AND DISCUSSION

Viscosity and molecular weight data for the five CTP fractions studied are shown in Table 1. Fractions 1, 3, 4 and 5

were obtained by precipitation from acetone and fraction 2 from propionic acid solution. In this latter case the  $\bar{M}_w/\bar{M}_n$  ratio was estimated by graphical interpolation and may be less reliable, although this is certainly not apparent from the good log  $[\eta]$  *versus* log  $\bar{M}_w$  plot obtained.

Corresponding double logarithmic plots of LVN *versus*  $\bar{M}_n$  and  $\bar{M}_w$  are shown in Figure 1. The good linear plots obtained illustrate the satisfactory applicability of the Mark–Houwink relationship for CTP over the molecular weight ranges investigated. It must also be concluded that the different  $\bar{M}_v:\bar{M}_n$  and  $\bar{M}_v:\bar{M}_w$  ratios each remain virtually constant for all the CTP fractions. Any differences between the viscosity-average and the number-average or weight-average molecular weights are incorporated in the corresponding *K* values.

Least squares treatment of the plots in Figure 1 provide the following Mark–Houwink relationships for  $\bar{M}_n$  and  $\bar{M}_w$  for CTP in chloroform at 25°C:

$$[\eta] = 1.67 \times 10^{-5} (\bar{M}_n)^{0.957} \quad (1)$$

$$[\eta] = 3.66 \times 10^{-5} (\bar{M}_w)^{0.877} \quad (2)$$

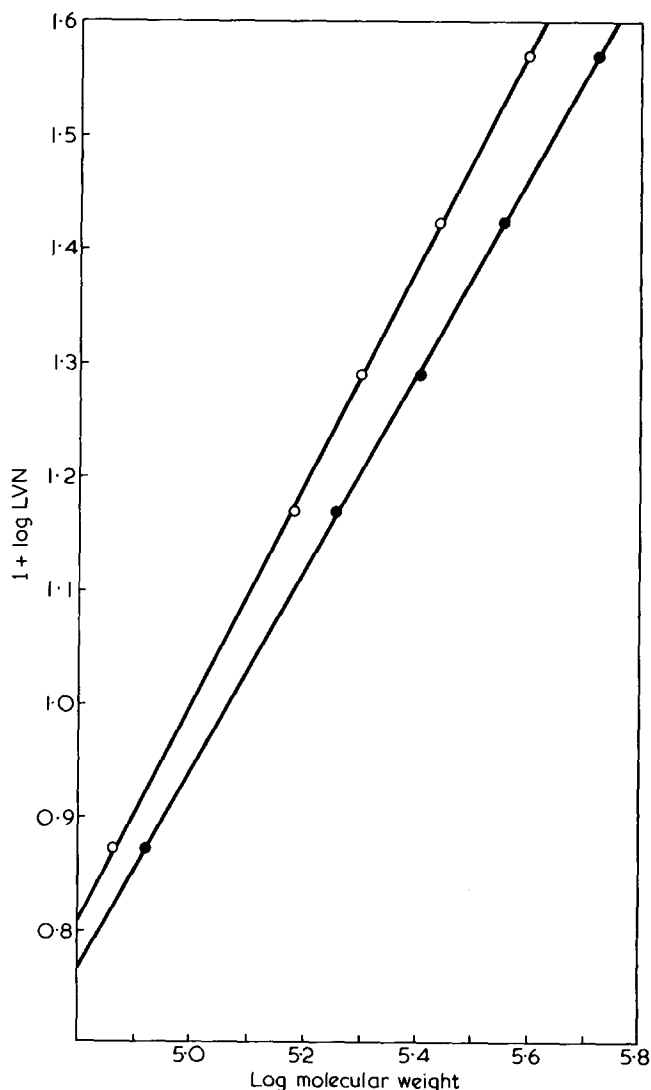


Figure 1 Logarithmic plots of limiting viscosity number *versus* molecular weight for cellulose tripropionate in chloroform at 25°C. O, number-average molecular weight; ●, weight-average molecular weight

Comparison of experimental  $\bar{M}_n$  and  $\bar{M}_w$  values (Table 1) with those calculated using the above relationships justified the expression of  $a$  values to three significant figures. Thus the average deviation of calculated from experimental molecular weight values using equations (1) and (2) was 1%. Rounding up the  $a$  values to 0.96 and 0.88 gave corresponding deviations of 4.3 and 5.0%, respectively. We therefore consider these relationships to be adequate for evaluation of molecular weights from  $LVN$  data within the molecular weight range  $70 \times 10^3$  to  $500 \times 10^3$  (degree of polymerization 200–1500 glucosidic units). Uncertainties in these calculated molecular weights should then be comparable with those found in the usual absolute methods employed.

The relatively high values for the Mark–Houwink exponent,  $a$ , found in the present work, indicates a high degree of chain extension for CTP in chloroform. This is in keeping with the greater stiffness shown by chains of cellulose derivatives in solution. Since values for  $a$  of between 0.95 and 1.02 have been reported<sup>4–6</sup> for cellulose triacetate in the same solvent it would appear that cellulose tripropionate chains are somewhat more flexible. A comparison could not be made with cellulose tributyrate since  $K$  and  $a$  values for chloroform have not so far been reported for this polymer.

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