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Poly(trimethylene terephthalate) molecular weight and Mark–Houwink equation

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Abstract

The Mark–Houwink equations relating the intrinsic viscosity of poly(trimethylene terephthalate) to its number and weight average molecular weights in two solvents are reported. Several simplified equations for single-point measurements are evaluated. The limit and accuracy of applicable equations are discussed. © 2001 Elsevier Science Ltd. All rights reserved.

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Poly(trimethylene terephthalate) (PTT) is a newly commercialized aromatic polyester. Although first synthesized by Whinfield and Dickson in 1941 [1] it remained an obscure polymer because one of its raw materials, 1,3-propanediol (PDO), was not readily available. Since its commercial introduction in 1998 there has been an increased interest in PTT for fiber, film and engineering thermoplastics applications [2].

As a norm, the polyester industry reports polymer molecular weights by the intrinsic viscosity (IV), also called the limiting viscosity number (LVN), denoted by $[\eta]$. It is related to the molecular weight, M, through the Mark–Houwink equation:

$$[\eta] = KM^{\alpha} \tag{1}$$

K and α are constants specific to the solvent and temperature used in the measurements. For PET and poly(butylene terephthalate) these constants are readily available and are well tabulated in the Polymer handbook [3] for a large number of solvents, temperatures and methods of molecular weight determination. However, this is not the case for PTT. Traub et al. [4] appeared to be the only ones to report PTTs K and α for a 1:1 (w/w) tetrachloroethane/phenol mixed solvent.

PTT is a fast crystallizing polymer. The rate is about an order of magnitude faster than PET [5]. Therefore a melt quenched PTT typically has crystallinity in the range of about 15–30 wt.%, which makes it more difficult to dissolve in solvents commonly used for amorphous PET. We found PTT to dissolve quite readily in hexafluoroisopronanol (HFIPA) or in a 1:1 mixture of trifluoroacetic acid and methylene chloride at room temperature. Typically the solution is ready for IV measurements in less than 2 h instead of overnight. However, HFIPA is a very expensive solvent for routine IV measurements, and methylene chloride is quite volatile to maintain in a 1:1 mixture with trifluoroacetic acid at elevated temperature or in prolonged storage. We also found PTT to dissolve within 30 min when heated to 110°C in a 60:40 mixture of phenol/tetrachloroethane, which is a workhorse solvent used in the PET industry. In this article, we report PTT's Mark–Houwink constants in HFIPA and in 60:40 phenol/tetrachloroethane, and discuss the applicability of the single-point IV method for this polymer.

PTT was synthesized by the transesterification of PDO and dimethyl terephthalate in the melt at 180–200°C using zinc acetate dihydrate catalyst. After transesterification was completed, the temperature was raised to 265°C and the melt polymerized under a vacuum of <0.3 mmHg using titanium butoxide catalyst to an M_w of 10,000–43,000. The polydispersity of the polymers agreed well with the theoretical M_w distribution of 2 for the polycondensation polymer.

Solution viscosities were measured in an Ubbelohde viscometer in three concentrations and in triplicates. IV was obtained by extrapolating the Huggins plot to zero concentration [6]. M_n was measured by titrating the polymer solution for hydroxyl end-groups according to the method described by Conix [7]. M_w was measured by small-angle

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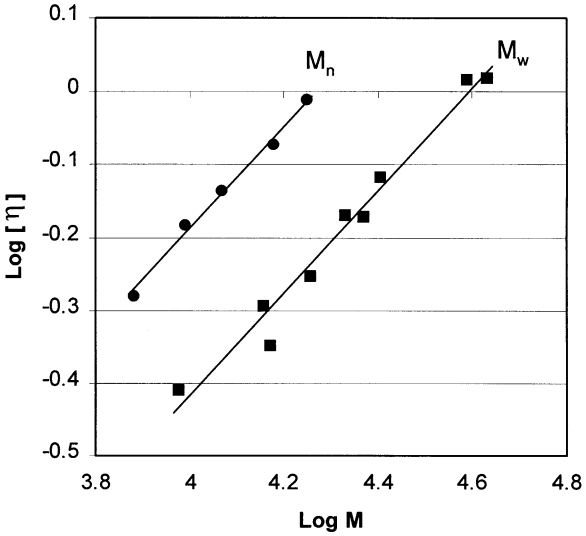

Fig. 1. Mark–Houwink plots of PTT M_n and M_w in HFIPA.

light scattering (SALS) using a KMX6 photometer and from Zimm plots. A C.N. Woods differential refractometer was used to measure the refractive index differentials for PTT in HFIPA. In single-point IV measurement, an automated Viscotek 501Y capillary relative viscometer was used. Fig. 1 shows the Mark–Houwink plots for PTT in HFIPA for both M_n and M_w. The constants, K and α obtained by linear regression of the plots are shown in Table 1.

In standard IV measurements, the solution viscosity is measured in at least three different concentrations and in triplicates for extrapolation of the Huggins or Kraemer plots to infinite dilution. Therefore, the method is quite laborious and time consuming. Several equations [8–11] have been developed such that IV can be estimated by just measuring the solution's specific viscosity, η_{sp}, or relative viscosity, η_{rel}, at only one specific concentration. Such estimation greatly simplifies IV measurements and is called the single-point method. Chee [12] critically examined these methods and found some of them to be inadequate or applicable to only specific polymer–solvent systems. Rao and Yaseen [11] reached similar conclusions in their analysis of the applicability of single-point equations for linseed oil-alkyd in solvents with various solubility parameters, from good to poor solvents. We examined some of the single-point equations (Eqs. (2)–(4) from Refs. [8–10], respectively), in HFIPA solvent and verified which one could be best used for PTT:

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_{rel})}}{c} \tag{2}$$

$$[\eta] = \frac{(\eta_{sp} + 3 \ln \eta_{rel})}{4c} \tag{3}$$

$$[\eta] = \frac{\eta_{sp} + \gamma \ln \eta_{rel}}{(1 + \gamma)c} \tag{4}$$

where

$$\gamma = \frac{k'}{k''}$$

k' and k'' are constants obtained from the Huggins and Kraemer plots, and are independent of the molecular weights [11];

$$[\eta] = \frac{(\eta_{sp} + \ln \eta_{rel})}{2c} \tag{5}$$

Table 2 compares the IV obtained from the Huggins and Kraemer plots [5] and single-point IV obtained from Eqs. (2)–(5). Although the Huggins and Kraemer equations are routinely used for accurate determination of $[\eta]$, we found that for PTT, the Kraemer equation consistently gave a slightly lower IV than the Huggins equation by about 0.5%. Rao and Yaseen also found that the graphical solution of the Huggins or Kraemer plots does not necessarily provide a more accurate $[\eta]$ than that calculated from single relative viscosity.

We found that the above four single-point equations worked fairly well in estimating PTT's $[\eta]$. Linear regressions R^2 of single-point $[\eta]$ with $[\eta]$ obtained by the Huggins and Kraemer equations were ≥ 0.996. When the solution concentrations were kept low with η_{sp} between 0.15 and 0.30, all four equations gave a reasonably good estimation of $[\eta]$ to within $\pm 3\%$. We were surprised to find that Maron's equation which requires measurements of the Huggins k' and the Kraemer k'', gave the same level of $[\eta]$ estimation accuracy over a rather wide range of η_{sp} between 0.12 and 0.65.

Table 1
PTT Mark–Houwink constants, K and α

Solvent	Temperature (°C)	Molecular weight determination method	$K \times 10^4$ (dl/g)	α
HFIPA	35	SALS	5.51	0.71
HFIPA	35	Hydroxyl group	10.0	0.70
60/40 Phenol/tetrachloroethane	30	SALS	5.36	0.69
50/50 Tetrachloroethane/phenol [4]	20	SALS	8.2	0.63

Table 2
Comparison of calculated $[\eta]$ with extrapolated values from the Huggins and Kraemer equations

$[\eta]_{sp}$	$[\eta]$					
	Huggins	Kraemer	Solomon and Sciuta [8]	Kuwahara [9]	Maron [10]	Rao and Yaseen [11]
0.644	1.046	1.039	1.058	1.048	1.035	
0.309			1.017	1.002	1.066	
0.164			1.021	1.015	1.025	1.034
0.594	0.977	0.972	0.950	0.937	0.974	
0.280			0.966	0.958	0.977	
0.154			0.967	0.961	0.972	0.980
0.593	0.961	0.957	0.954	0.949	0.959	
0.277			0.952	0.928	0.959	
0.153			0.942	0.944	0.958	0.950
0.463	0.784	0.781	0.775	0.772	0.784	
0.221			0.759	0.750	0.782	
0.123			0.773	0.767	0.782	0.772
0.407	0.698	0.694	0.707	0.702	0.691	
0.202			0.673	0.665	0.716	
0.108			0.678	0.675	0.682	0.675
0.323	0.557	0.557	0.558	0.561	0.555	
0.156			0.565	0.553	0.562	
0.085			0.545	0.552	0.552	0.552

This is probably due to the equation derived from both Huggins and Kraemer equations with a priori known k' and k''.

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