Molecular Weight–Viscosity Relationships for Poly(1,4-butylene Terephthalate)

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Synopsis

The correlation between number-average molecular weight and intrinsic viscosity in 60:40 phenol-*sym*-tetrachloroethane at 30°C for poly(1,4-butylene terephthalate) was established from endgroup determinations as well as by gel permeation chromatography, eqs. (1) and (10a). The GPC data also yielded relationships between weight- and z-average molecular weight and intrinsic viscosity, eqs. (10b) and (10c). Melt viscosities, corrected for the thermal history of the melt, were measured at shear stresses in the range of 0.02–0.55 MPa. Linear PBT melts were found to become non-Newtonian at a shear stress of approximately 0.11 MPa, independent of molecular weight within the range studied. Correlations between melt viscosity at low shear stress versus intrinsic viscosity are presented, as well as the dependence of melt viscosity in the non-Newtonian region on shear stress and low-stress (Newtonian) melt viscosity.

INTRODUCTION

During the first half of this decade, poly(1,4-butylene terephthalate) (PBT) has rapidly gained increasing commercial importance as a thermoplastic injection molding resin. Poly(ethylene terephthalate), though similar chemically, is less suitable for injection molding use because of much lower crystallization rates but has been in extensive commercial use for several decades in fiber and film applications.

While viscosity–molecular weight relationships for PET have been reported by several investigators,[1-3] considerably less has been reported about poly(1,4-butylene terephthalate).[4] This article describes our results in establishing relationships between the molecular weight of poly(1,4-butylene terephthalate) and its intrinsic and melt viscosities.

EXPERIMENTAL

Sample Preparation

Poly(1,4-butylene terephthalate) samples were prepared by titanium ester catalyzed ester interchange reaction between dimethyl terephthalate and 1,4-butanediol at 170°–230°C, followed by polymerization at 250°–255°C and 0.1 mm Hg until the desired molecular weight was obtained.

Endgroup Determination

To determine combined hydroxyl and carboxyl endgroups, the sample was first acylated with succinic anhydride in nitrobenzene solution at 150°C. Addition of 5% pyridine to the nitrobenzene greatly accelerated the rate of acylation.

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The product was precipitated, washed successively with methanol and chloroform, and vacuum dried for at least 4 hr at 110°C.

To determine the combined carboxyl endgroups, the acylated polymer sample was dissolved in hot benzyl alcohol, and the solution was cooled and diluted with chloroform, followed by titration in a nitrogen atmosphere with 0.05N NaOH in benzyl alcohol against a phenol red indicator.

Number-average molecular weight M_n of the polymer was calculated from the total endgroup concentration N (expressed in meq/kg) by

$$M_n = \frac{2 \times 10^6}{N}$$

Gel Permeation Chromatography

Gel permeation chromatograms were determined with a Waters Associates instrument equipped with crosslinked polystyrene columns of pore sizes 10^6, 10^5, 3×10^3, and 250 Å, respectively. (The GPC curves were determined by personnel and in the facilities of DeBell and Richardson, Inc., Hazardville, Connecticut, under the direction of Dr. M. Ezrin.) Determinations were performed on 0.5% solutions in m-cresol, stabilized with 0.5% benzoic acid, at 100°C. Injection time was 60 sec, and the flow rate was 1 ml/min.

Total analysis time, including the time required to dissolve the sample, was approximately 4 hr. During that period of time, the relative viscosity of the solution remained constant within experimental error, indicating negligible degradation of the sample.

The gel permeation columns were calibrated with narrow molecular weight distribution polystyrene standards (Pressure Chemical Company) dissolved in benzoic acid-stabilized m-cresol at 100°C.

Intrinsic Viscosity Determinations

Intrinsic viscosities of the polystyrene standards and the PBT samples in m-cresol at 100°C were determined in a capillary solution viscometer of the dilution type by extrapolation to zero concentration of specific viscosity measurements obtained at four different concentration levels. In addition, the intrinsic viscosity of the PBT samples was determined in a 60:40 w/w solvent mixture of phenol and tetrachloroethane at 30°C.

Melt Viscosity Determinations

Melt viscosities were determined with an automatic capillary rheometer Model 3501-M, manufactured by the Monsanto Research Corporation. A range of piston loadings and capillaries of various dimensions were used to cover a wide range of shear stresses.

The equipment automatically repeats a melt viscosity determination at adjustable, preset time intervals (5, 10, 15, and 20 min are suitable values). This allows back extrapolation of the data to zero heating time to eliminate the effects of thermal history on the melt viscosity of the sample.

Provided the samples were carefully dried (minimum drying conditions were

4 hr at 110°C in a vacuum desiccator), it was possible to obtain a straight-line back extrapolation of the data on a plot of log melt viscosity versus heating time. The slope of the line depended on temperature only and varied little from sample to sample.

RESULTS

M_n–Intrinsic Viscosity Relations by Endgroup Count

Number-average molecular weight M_n, as calculated from the endgroup determination, and intrinsic viscosity in 60:40 phenol–tetrachloroethane at 30°C were determined for 25 samples ranging in intrinsic viscosity from 0.09 to 1.33 dl/g. A double logarithmic plot of the data is shown in Figure 1. Regression analysis of the data yielded

$$IV_{pt} = 1.166 \times 10^{-4} M_n^{0.871} \tag{1}$$

where IV_{pt} = intrinsic viscosity measured in 60:40 phenol–tetrachloroethane at 30°C, and M_n = number-average molecular weight. Standard deviation of the data points was ±11.3%.

Molecular Weight–Intrinsic Viscosity Relations (GPC)

The "Universal Calibration Method" of Benoit et al.[5] was used to evaluate the gel permeation chromatograms of six PBT samples ranging in intrinsic viscosity from 0.264 to 1.326 dl/g, as determined in 60:40 phenol–tetrachloroethane solution at 30°C.
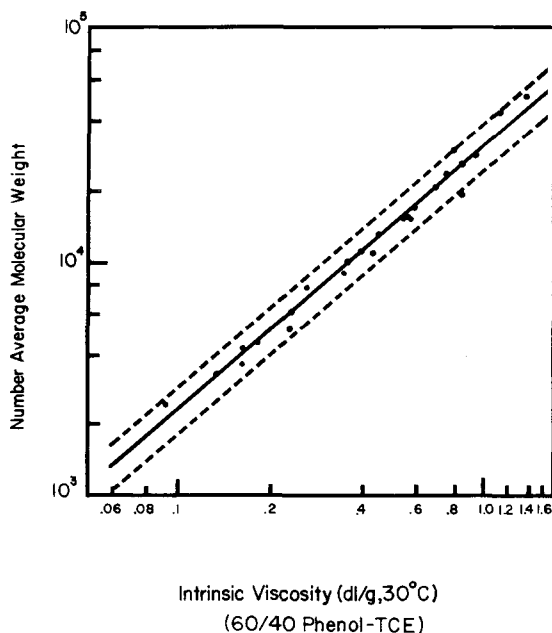

Fig. 1. Number-average molecular weight, calculated from endgroup determinations, vs intrinsic viscosity in 60:40 w/w phenol–*sym*-tetrachloroethane solution at 30°C: (—) best fit through the data points; (- - -) 2 standard deviation error limits (±23%) for individual data points.

The universal calibration method rests on the assumption that GPC elution volume V_E is a function of the product of molecular weight and intrinsic viscosity, independent of the chemical nature of the polymer sample:

$$V_E = f(M \times IV) \tag{2}$$

Especially in the case of linear polymers this assumption has been verified in numerous instances with a wide variety of materials.[6] The GPC columns can, therefore, be calibrated in terms of $M \times IV$ through the use of readily available, carefully characterized polymer standards of narrow molecular weight distribution, such as the polystyrene standards provided by the Pressure Chemical Company. Combination of (2) with the Mark-Houwink relationship for PBT,

$$IV = KM^a \tag{3}$$

where K and a are empirical constants yet to be determined, allows elimination of the IV variable to arrive at the required calibration equation of M in terms of V_E necessary to interpret the gel permeation chromatograms.

Equation (3) is similar to eq. (1), except that the IV in eq. (3) refers to the solution of PBT in m-cresol at 100°C and that M (for monodisperse polymer) is used instead of M_n. The necessary conversions were made as follows: The relationship between intrinsic viscosities determined in 60:40 phenol–tetrachloroethane at 30°C (IV_{pt}) and in m-cresol at 100°C (IV_{mc}) was calculated from experimental values determined on a number of PBT samples of varying viscosity:

$$IV_{mc} = 0.7256 \, IV_{pt}^{0.972} \tag{4}$$

Combination of eqs. (4) and (1) then yielded

$$IV_{mc} = 1.09 \times 10^{-4} \, M_n{}^{0.847} \tag{5}$$

To convert eq. (5) to eq. (3), a method was used as proposed by Shultz et al.[7] Under the assumption that the molecular weight distributions of the polyester samples could be described by the equation of Schulz[8] and Zimm,[9] the exponent in (5) is equal to the constant a in eq. (3).

The constant K in eq. (3) is related to the constant in (5) by

$$K = \frac{z^a \Gamma(z + 1)}{\Gamma(z + a + 1)} \, (1.09 \times 10^{-4}) \tag{6}$$

where K and a are the parameters of eq. (3), Γ represents the gamma function, and z is a parameter in the Schulz-Zimm equation related to the molecular weight distribution, with $z = 1$ for a "most probable" molecular weight distribution.

Under the assumption that the polyester samples had such a nearly "normal" molecular weight distribution, an assumption subsequently borne out by the GPC results shown below, $z = 1$ was substituted in eq. (6), resulting in $K = 6.25 \times 10^{-5}$ and

$$IV_{mc} = 6.25 \times 10^{-5} \, M^{0.847} \tag{7}$$

The GPC columns were calibrated in terms of elution volume versus $(M \times IV)$ with polystyrene standards in m-cresol at 100°C. The data could be described with good accuracy by the empirical equation

$$\log (M \times IV) = 22.8242 - 0.9749 V_E + (9.471 \times 10^{-3} V_E{}^2) \tag{8}$$

where V_E represents elution volume and IV is the intrinsic viscosity of the standards as measured in m-cresol solution at 100°C.

Combining eqs. (7) and (8) yielded the calibration eq. (9) used for numerical integration of the GPC curves for the PBT samples:

$$\log M = 14.634 - 0.5278V_E + (5.128 \times 10^{-3}V_E{}^2) \tag{9}$$

The results are listed in Table I and illustrated graphically in Figure 2.

The lines drawn through the data points in Figure 2 are best fits obtained with the restraint that the exponent of the molecular weight variable in the Mark-Houwink equation should equal 0.871, as determined earlier by endgroup determinations, eq. (1). Figure 2 shows that this resulted in reasonable fits to the data. The resulting regression equations were:

$$IV = 1.29 \times 10^{-4}M_n{}^{0.871} \tag{10a}$$

$$IV = 7.39 \times 10^{-5}M_w{}^{0.871} \tag{10b}$$

$$IV = 4.85 \times 10^{-5}M_z{}^{0.871} \tag{10c}$$

TABLE I
GPC Results

IV_{pt}, dl/g	IV_{mc}, dl/g	M_n $\times 10^{-3}$	M_w $\times 10^{-3}$	M_z $\times 10^{-3}$	M_w/M_n	M_z/M_n
0.264	0.201	7.9	13.8	21.6	1.75	1.56
0.558	0.408	13.3	27.5	43.9	2.07	1.59
0.717	0.520	22.1	38.6	59.9	1.74	1.55
0.910	0.669	27.3	49.5	79.3	1.81	1.60
1.087	0.761	30.9	59.1	100.9	1.90	1.70
1.326	0.985	33.5	69.6	119.0	2.07	1.70

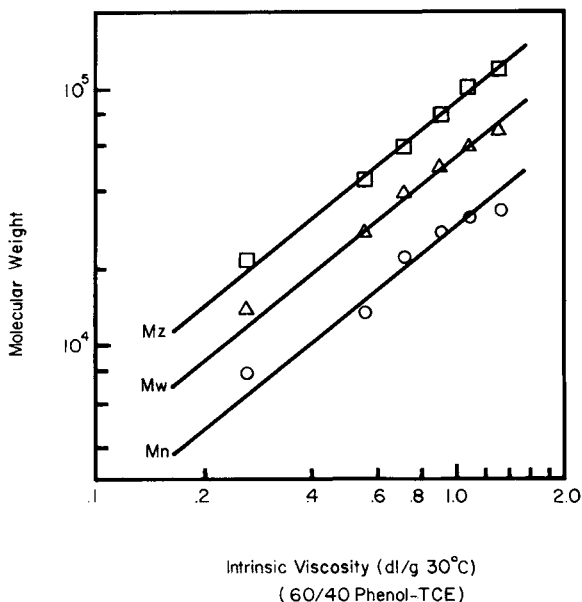Intrinsic Viscosity (dl/g 30°C)

(60/40 Phenol–TCE)

Fig. 2. Number-, weight-, and z-average molecular weights, determined by gel permeation chromatography, vs intrinsic viscosity: (O) number-average; (△) weight-average; (□) z-average molecular weight data.

From eqs. (10a) and (10b) follows $M_w/M_n = 1.9$, corresponding to $z = 1.1$ in the Schulz-Zimm equation. Repeating the calculations with $z = 1.1$ changed the molecular weights by less than 3% and did not affect the calculated M_w/M_n ratio.

Similarly, eqs. (10b) and (10c) yield $M_z/M_w = 1.6$. The difference between number-average molecular weights calculated from eqs. (1) and (10a) is 11%.

Melt Viscosity Versus Intrinsic Viscosity

PBT above its melting point undergoes slow thermal degradation resulting in a decrease in melt viscosity with time. This effect was compensated for by measuring the melt viscosity of the samples at several time intervals and extrapolating the data back to zero heating time. The extrapolation is linear on a log MV-versus-time plot; the slope of the semilog relationship for carefully dried samples depends only on the temperature and has a magnitude of $10^{-4} \sec^{-1}$ at 250°C.

Initial results indicated that at low shear stress ($<7 \times 10^4$ Pa) the melt viscosity MV_0 of linear PBT was Newtonian, i.e., independent of shear stress. Measurements of MV_0 (at 250°C) and intrinsic viscosity in (60:40 phenol–tetrachloroethane at 30°C) for a number of PBT samples yielded the following relationship:

$$MV_0 = 595 \, IV_{pt}^{5.53} \qquad (Pa \cdot s) \tag{11}$$

The data are illustrated in Figure 3.

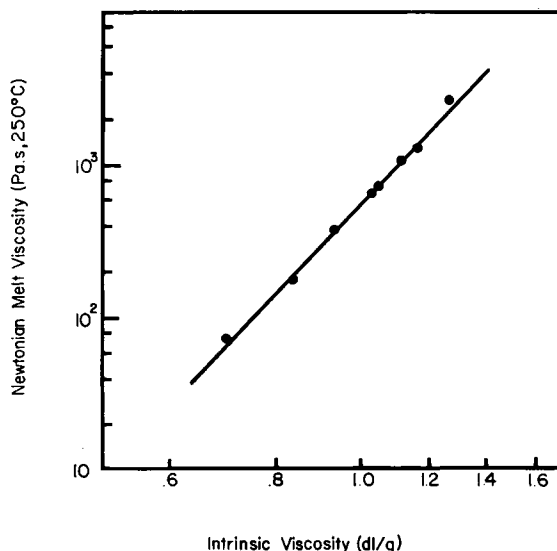Fig. 3. Melt viscosity at low shear stress (<0.07 MPa), corrected for thermal history of the melt, vs intrinsic viscosity.
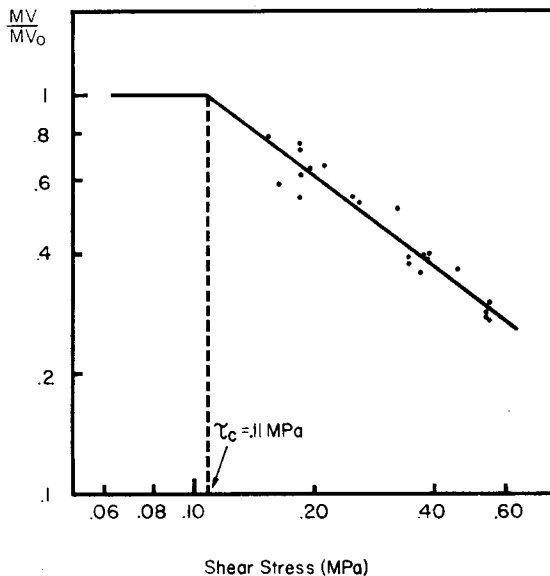
Fig. 4. Melt viscosity reduction vs shear stress at 250°C in the non-Newtonian stress region. MV_0 = Melt viscosity at low shear stress.

Non-Newtonian Melt Viscosity

Above a critical shear stress τ_c, PBT melts become non-Newtonian. Assuming that above τ_c the melts obey the power law

$$\tau = K\dot{\gamma}^n \qquad \tau > \tau_c \tag{12}$$

where τ = shear stress, $\dot{\gamma}$ = shear rate, and K = constant, we find

$$MV = \frac{\tau}{\dot{\gamma}} = K^{1/n} \cdot \tau^{1-(1/n)} \tag{13}$$

At the critical shear stress,

$$MV_c = MV_0 = K^{1/n} \cdot \tau_c^{1-(1/n)} \tag{14}$$

Combining eqs. (13) and (14) and taking logarithms yields

$$\log (MV/MV_0) = -(1 - 1/n) \log \tau_c + (1 - 1/n) \cdot \log \tau \tag{15}*$$

A plot of $\log (MV/MV_0)$ versus $\log \tau$ for a number of PBT samples of varying melt viscosities is shown in Figure 4. The slope of the line that best fits the data was found to be -0.77, corresponding to a value $n = 0.57$ in the power equation (12). Evaluation of the constant factor in eq. (15) yielded $\tau_c = 1.08 \times 10^5$ Pa.

In practice, the critical shear stress is an idealized point found by extrapolation of the Newtonian and non-Newtonian branches of the log shear stress–log shear rate relationship until they intersect. The actual transition to non-Newtonian melt behavior occurs gradually in the shear stress range of $(0.7–1.4) \times 10^5$ Pa (10–20 psi). As a result, a typical commercial grade of PBT with a Newtonian melt viscosity in the range of 600–700 Pa·s will become non-Newtonian at shear rates above approximately 100 sec^{-1}.

* In this derivation it is implicitly assumed that, at a given shear stress, MV is directly proportional to MV_0 for samples of different molecular weights. Multiple regression of the data actually yielded a proportionality of MV to $MV_0^{0.944}$, but the improvement in the fit of the data due to this refinement was statistically insignificant.

Substitution of $\tau_c = 1.08 \times 10^5$ Pa and $n = 0.57$ in eq. (15) and rearranging yields

$$MV = 7500\ MV_0 \tau^{-0.77} \qquad (\text{Pa·s}, 250°\text{C}) \tag{16}$$

Substitution of $\tau = \dot{\gamma} \cdot MV$ and rearranging terms yields the melt viscosity in the non-Newtonian region in terms of the Newtonian viscosity and shear rate:

$$MV = 155\ MV_0^{0.57} \dot{\gamma}^{-0.44} \qquad (\text{Pa·s}, 250°\text{C}) \tag{17}$$

Temperature Dependence of Melt Viscosity

Measurements in the temperature range of 240°–275° indicate that the melt viscosity at low shear stress is proportional to $\exp(5100/T)$, where $T =$ the temperature of the melt in kelvins. It should be noted, however, that 275°C is considerably above the normal processing temperature for this material as recommended by the manufacturers; at this temperature, time-dependent changes in viscosity due to thermal degradation during the residence times normally encountered in plastics processing equipment are considerably greater than the change in melt viscosity due to the higher temperature alone.

If we include the temperature proportionality factor in eq. (11), we obtain

$$MV_0 = 3.46 \times 10^{-2} \exp(5100/T)\ IV_{pt}^{5.53} \qquad (\text{Pa·s}) \tag{18}$$

where as before MV_0 denotes the melt viscosity, at sufficiently low shear stress that the melt behaves as a Newtonian liquid, extrapolated to zero heating time to compensate for the thermal history of the sample.

References

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