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The linear master dependence for polymer melts in the non-Newtonian range

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SUMMARY

The multivariable power function $\Delta\varphi\cdot\eta_0=B(\dot{\gamma}\eta_0)^{b_1}\cdot q^{b_2}\cdot G^{b_3}$ (symbols are explained in the text) is proposed as the general linear master dependence for the behaviour of linear and branched polymer melts in the non-Newtonian range. It can be applied for generation of any flow curve for a given polymer sample provided that constants B, b_1, b_2 and b_3 are known. It has been found, using the experimental data on polycarbonate, that B is approximately equal to 3×10^{-5} being the universal constant, and $b_1=0.77$ for linear polymers. Lower values of b_1 indicate the existence of branched macromolecules, and the relationship of b_1 vs G can be used for determination of branching degrees from the rheological data.

INTRODUCTION

The application of the general approach to polymer properties dependent on molecular characteristics (1) has led to the following multivariable power function for polymer melts in the non-Newtonian range (2)

$$\Delta\varphi = B\cdot\dot{\gamma}^{b_1}\cdot q^{b_2}\cdot G^{b_3}\cdot\eta_0^{b_4} \qquad (1)$$

where $\Delta\varphi$ is the deviation of polymer fluidity from the Newtonian conditions

$$\Delta\varphi = 1/\eta - 1/\eta_0 \qquad (2)$$

η and η_0 being the polymer melt viscosities at a given shear rate $\dot{\gamma}>0$ and at zero shear rate $\dot{\gamma}=0$, respectively, q is the polydispersity degree defined by the ratio of weight- to number-average molecular weights, $q=M_w/M_n$, and G is the branching degree defined by the ratio of intrinsic viscosities of branched (br) and linear (lin) molecules, $G=[\eta]_{br}/[\eta]_{lin}$. Thus, the influence of $\dot{\gamma}$ is taken into account simultaneously with the influence of molecular characteristics such as average molecular weights M_x, molecular weight distribution (MWD) and long chain branching (LCB). The influence of M_x is included into the value of η_0 since the following relation holds (2,3)

$$\eta_0 = K_m\cdot M_x^{a_1}\cdot q^{a_{2,x}}\cdot G^{a_3} \qquad (3)$$

The values of B, b_1, b_2, b_3 and b_4 are characteristic constants, where $b_4 = b_1 - 1$, cf.(2).

The commonly used master curves for the melt flow properties of polymers, i.e. the plots of log η/η_0 vs log $\dot{\gamma}\eta_0$ can be derived from eqs.(1) and (2), cf.ref.(3)

$$\eta/\eta_0 = 1/[K_B(\dot{\gamma}\eta_0)^{b_1} + 1] \qquad (4)$$

where

$$K_B = B.q^{b_2}.G^{b_3} \qquad (4a)$$

However, linear and branched polymers are represented by different master curves shifted according to the branching degrees (2,3).

In this paper a linear form of the polymer melt viscosity dependence on the shear rate is proposed as the general master straight line for all polymer melts.

LINEARIZATION OF FLOW CURVES

It has been found that eq.(1) leads also to linear relationships in log-log coordinates such as

$$\Delta\varphi = K.\dot{\gamma}^{b_1} \qquad (5)$$

where

$$K = B.q^{b_2}.G^{b_3}.\eta_0^{b_4} \qquad (5a)$$

or

$$\Delta\varphi.\eta_0 = K_B(\dot{\gamma}\eta_0)^{b_1} \qquad (6)$$

where K_B is given by eq.(4a), and

$$\Delta\varphi.\eta_0 = (\eta_0/\eta) - 1 \qquad (6a)$$

Thus, various straight lines in log-log coordinates are obtained for samples of different branching degree using eq.(5), cf.ref.(3), or eq.(6), cf.ref.(2). The appropriate arrangement of variables gives the following equation

$$\Delta\varphi.\eta_0 = B(\dot{\gamma}\eta_0)^{b_1}.q^{b_2}.G^{b_3} \qquad (7)$$

which is represented by only one straight line in log-log coordinates as the plot of $Y = \log \Delta\varphi.\eta_0$ vs $X = \log(\dot{\gamma}\eta_0)^{b_1}.q^{b_2}.G^{b_3}$. It should be valid not only for linear and branched samples of a given polymer but also for different linear and branched polymers.

EXPERIMENTAL

Linear and branched bisphenol A polycarbonate (PC) samples were prepared by interfacial polycondensation as described elsewhere (2,4). Commercial samples of Makrolon (Bayer AG), Lexan (General Electric Co.), and Bistan (Zachem, Poland) were also used. The samples were characterized by their average molecular weights M_x, the polydispersity degree q as a measure of MWD, and the branching degree G as a measure of LCB. The gel permeation chromatography and viscometric methods were used for molecular characterization of PC samples (4). Melt viscosities were measured at 553 K (280°C) using a MCR Instron capillary rheometer (2,5).

RESULTS AND DISCUSSION

Molecular characteristics of PC samples, as well as their zero shear rate melt viscosities η_0 are given in Table 1.

Table 1
Characteristics of PC samples

Sample no.	M_wx10^{-3}	q	G	η_0, Pa.s	b_1	
					found	eq.(8)
1	26.1	2.1	1.00	360	0.77	0.77
2	33.7	4.3	1.00	1200	0.77	0.77
3	42.2	3.3	0.83	2100	0.70	0.69
4	59.3	3.9	0.82	9600	0.66	0.68
5	63.7	5.3	0.63	3600	0.60	0.60

The constants b_1, b_2, and b_3, needed for eq.(7), can be determined from regression equations for eqs.(5) or (6), using statistical procedures for experimental data. The values of b_1, see Table 1, are consistent with the relation found earlier for PC (2)

$$b_1 = 0.30 + 0.47\ G \qquad (8)$$

Eq.(8) can be used for determination of branching degree G of PC samples from the rheological data. For other polymers, coefficients of relationship of b_1 vs G should be find, e.g. according to the procedure described for PC (2). It should be noted that the value of b_1=0.77 found for linear samples from the experimental data agrees with the theoretical value of b_1=0.767 found from the theoretical approach of Graessley (6), for the parameter Z=1 of the exponential MWD function, cf.(2), i.e. for the most probable MWD with q=2. The values of b_2=0 and b_3=-8 are taken for PC samples in this work as it has been determined earlier (2).

The plot of Y vs X for PC, according to eq.(7), is shown in Figure 1. The correlation of experimental data has been estimated by the following relationship

$$Y = \log B + A.X \qquad (9)$$

where the slope A should be equal to unity. The results are

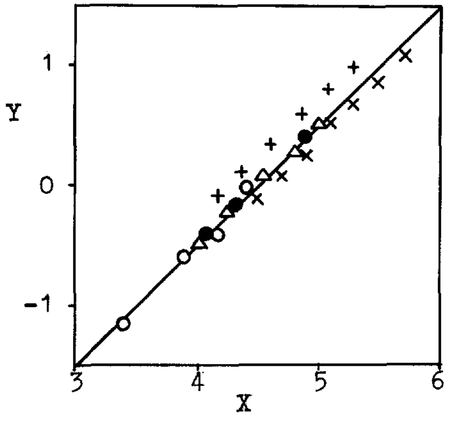

Figure 1. The general master dependence for polymer melts. Experimental data for PC samples: 1 (o), 2 (●), 3 (△), 4 (+), and 5 (x).

shown in Table 2. Thus, excellent correlation is obtained for linear PC samples and quite good correlation for linear and branched PC samples, in spite of possible errors in measurements of rheological data as well as in molecular characteristics of a branched polymer.

Table 2
Correlation of experimental data for PC

Samples	No. of points	A	$Bx10^5$	Correlation coefficient r^2
PC: lin	7	1.02	2.4	0.998
PC: lin+br	25	0.97	4.7	0.929

The constant B is considered as the universal one for all polymer melts. The precise value of B should, however, be find also for other linear and branched polymers for which reliable rheological and molecular characteristics should be measured. We have tried to use some other experimental data on branched PC (7) and recently published data on polyethylene (PE)(8), although they are unsufficient for statistical treatments. Nevertheless, it seems that the results of final calculations according to eq.(6) with assumed b_2=0 for the literature data (7,8), as well as the results of calculations for PC of this work according to the same procedure, confirm the universality of the constant B, see Table 3. Thus, it can be suggested that the value of the universal constant B is of the order of $(3.0 \pm 1.5)x10^{-5}$.

Table 3
Determination of the constant B

Polymer Temp.,K	Reference for experimental data	Sample no.	Calculations				
			b_1	G	K_Bx10^{+5}	$Bx10^5$	r^2
PC 573	Idel et al.(7)	1	0.686	0.82	27	1.8	0.968
		2	0.675	0.80	23		
		3	0.756	0.97	2.6		
PE 453	Acierno et al. (8)	H	0.774	0.96	1.9	1.6	0.995
		L1	0.635	0.31	360		
		L2	0.640	0.30	280		
PC 553	this work	1	0.77	1.00	2.9	3.5	0.950
		2	0.77	1.00	3.1		
		3	0.70	0.83	15		
		4	0.66	0.82	29		
		5	0.60	0.63	98		

Therefore, every melt flow curve for every polymer can be obtained from the general master straight line, eq.(7), see Figure 1, if the exponents b_1, b_2, and b_3, as well as molecular characteristics q and G are known for a given polymer sample. For PC b_2=0 and the values of q are not needed in this case.

The value of $b_1=0.77$, or at least $b_1=0.76\pm0.01$, is valid for all linear polymers. It has been found experimentally, cf. Table 3, see also (2), and it is consistent with the theory of Graessley (6), cf.(2). Thus, for linear polymers we have

$$\Delta\varphi\cdot\eta_o = B(\dot{\gamma}\eta_o)^{b_1}\cdot q^{b_2} \qquad (10)$$

or

$$\Delta\varphi\cdot\eta_o = B(\dot{\gamma}\eta_o)^{b_1} \qquad (11)$$

if samples are monodisperse (q=1), or if for polydisperse polymer samples $b_2=0$ is found, as it is in the case of PC. Therefore, since the constants B and b_1 are known, the flow curve η vs $\dot{\gamma}$ can be generated from eqs.(10) or (11) for each linear polymer.

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