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The Effect of the Molecular Weight on the Glass Transition Temperature in Amorphous Poly(Ethylene Terephthalate)

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SUMMARY

The glass transition temperature of amorphous and fractionated poly(ethylene terephthalate) has been measured by differential scanning calorimetry. The application of the Fox-Flory equation for the range of molecular weights between 37100 and 4500 gives the values of $Tg_{\infty}=342.4$ K and Kg=51200. The low value of Kg is interpreted by the free volume theory. The flex energy of the chain is evaluated by the Gibbs-Di Marzio theory with a value of 1483 cal/mol. These results are compared with those obtained by other authors for the poly(ethylene adipate) and the poly(diethylene terephthalate).

INTRODUCTION

It is well known that the glass transition temperature Tg of a polymer depends on the length of the chain. One of the mostly used equations to study this relation was suggested by Fox and Flory (1):

$$Tg = Tg_{\infty} - \frac{Kg}{Mn} \qquad |1|$$

where Tg_{∞} is the glass transition temperature for an ideal chain of infinite length and Kg is a characteristic parameter of the dependence between Tg and Mn.

There are many polymers for which this dependence has been studied, such as polystyrene (1,2), poly(methyl methacrylate) (3,4), polyacrylonitrile (5,6), poly(vinyl chloride) (7), polypropylene (8,9), poly(dimethyl siloxane) (10) and poly(α-methyl styrene) (11). In the case of linear aliphatic and aromatic polyesters, this relation has been studied for the poly(ethylene adipate) (12) and poly(diethylene terephthalate) (13). This paper presents the results achieved with the poly(ethylene terephthalate) (PETP), whose Tg has been determined by differential scanning calorimetry.

According to Boyer (14) there is a correlation between the parameters Tg_{∞} and Kg. Polymers with higher Tg_{∞} show a high Kg, characteristic of stiff chain and/or high polarity, whilst polymers with low Tg_{∞} show, equally, a low Kg, characteristic of flexible chain and/or low polarity. Tg_{∞} and Kg values for PETP, partially deviate from the correlation proposed by Boyer. These results are discussed at the light of the free volume theory (15) and the Gibbs-Di Marzio theory (16) and compared to those obtained by other authors for the poly(ethylene adipate) (12) and the poly(diethylene terephthalate) (13).

EXPERIMENTAL

A commercial poly(ethylene terephthalate), fractionated by precipitation in the o-chlorophenol/n-hexane system at 25 °C (17), has been used. The intrinsic viscosity of each fraction has been determined in o-chlorophenol, at 25 °C. The average molecular weights above 10000 have been evaluated by the Moore and Sanderson equation (18):

$$|\eta| = 1.9 \times 10^{-4}\ Mn^{0.81}$$

whilst the molecular weights below 10000 by the so-called average equation (19) :

$$|\eta| = 2.9 \times 10^{-4}\ Mn^{0.76}$$

The glass transition temperatures have been determined in a Mettler TA 3000 Thermoanalyser, by the DSC 30 cell, with a heating rate of 10 K/min. Tests were carried out with amorphous PETP. For this reason, the polymer was melted at 280 °C for 10 minutes and then quenched by inmersion in liquid nitrogen. The cristallinity percentage calorimetrically measured was below 3 %.

Two DSC curves have been recorded for every sample. The first DSC curve has been obtained by heating at 10 K/min from 20 °C to 95-100 °C, followed by a fast cooling (approximately at 100 K/min) to 20°C. The second DSC curve was recorded using the same parameters as for the first. The glass

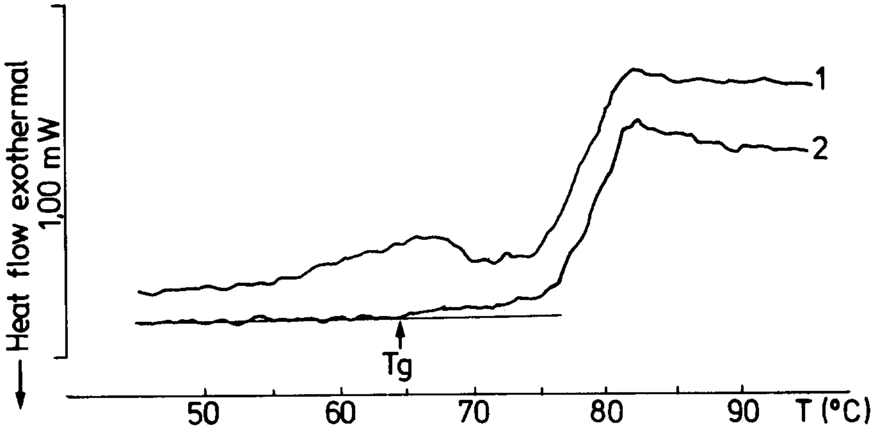

Figure 1. DSC curves for PETP (fraction number 7), with a heating rate of 10 K/min. The curve 1 corresponds to the first run and the curve 2 to the second one after a fast cooling of the sample.

Table 1. Glass transition temperature of fractionated amorphous poly(ethylene terephthalate)

Fraction	Mn	Tg (K)
1	37100	342.0
2	32000	341.6
3	27800	340.0
4	23400	339.8
5	19400	339.0
6	11750	337.7
7	9800	337.4
8	6850	334.5
9	6050	335.8
10	5100	331.2
11	4500	331.3

transition temperature has been determined on the second DSC curve with the purpose to prevent physical aging effects (figure 1). The temperature at which the DSC curve begins to deviate from the base line has been taken as Tg. Results are shown in table 1.

RESULTS AND DISCUSSION

Figure 2 shows the Tg variation versus the molecular weight; two zones are evidenced: one with a slight variation from Mn=37000 down to Mn=12000 and, another, with a deeper dependence below Mn=12000. The total Tg variation in the whole range of molecular weights studied was of 10.7 °C. This low value of the total Tg variation is also apparent in the low value of the Kg parameter of Fox-Flory equation. Representing Tg versus 1/Mn for

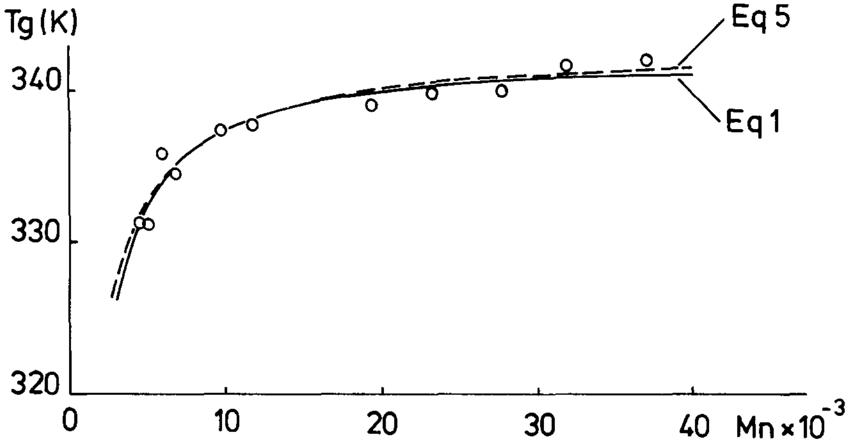

Figure 2. Dependence of Tg on molecular weight according to the Fox-Flory equation (Eq. 1) and the Gibbs-Di Marzio theory equation (Eq.5).

the PETP (figure 3), Tg_{∞} will be found 342.4 K and Kg 51200. Regresion line for all eleven points has been calculated from the above data giving a standard error of 0.9 K and a coefficient of determination r^2=0.944.

The results obtained by the Fox-Flory equation lead to a relatively low value of Kg. According to Boyer´s paper (14), concerning the correlation between Kg and Tg_{∞} , to a linear polymer with Tg_{∞} =342 K corresponds a Kg=130000 (figure 4). The experimental value found for the PETP is less than one half of the this figure. Considering only the fractions with Mn > 10000, Kg will be 69500, a value also far away from that estimated for Tg_{∞} =342 K.

Low Kg values are observed in other polyesters too; thus, from the results mentioned for both poly(ethylene adipate) (PEA) (12) and the poly(diethylene terephthalate) (PDETP) (13), the Kg values of 13200 and 45700, respectively, have been calculated applying Fox-Flory equation for the whole range of the experimental values (table 2).

According to the correlation of Boyer (14), polymers showing a high Tg_{∞} , have equally a high Kg due to the rigidity of the chain or to the high polarity of the macromolecule, whilst the contrary happens in polymers with flexible chain or very low polarity. This happens in the case of the PEA, for which a low value of Kg corresponds to a low value of Tg_{∞}.In PETP, although Kg value is low, suggesting a polymer with flexible chain, a moderately high Tg_{∞} is observed. In PDETP, the Tg_{∞} value is lower than in the PETP because the diethylene group confers a greater mobility to the chain.

There are a few theoretical attempts to interpret Kg values, one of them being based on the free volume concept applied by Bueche (15). This theory assumes that the free volume, at the glass transition temperature, is constant for samples of different molecular weight and also that each

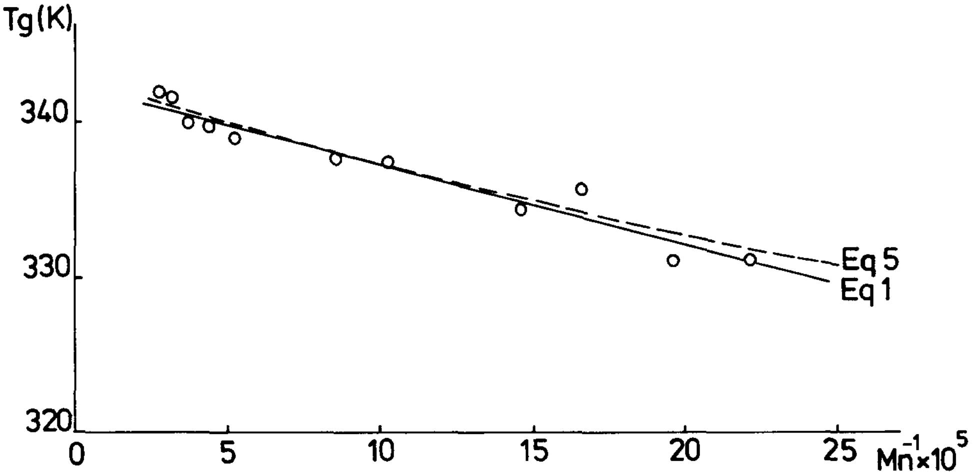

Figure 3. Dependence of Tg on reciprocal molecular weight.

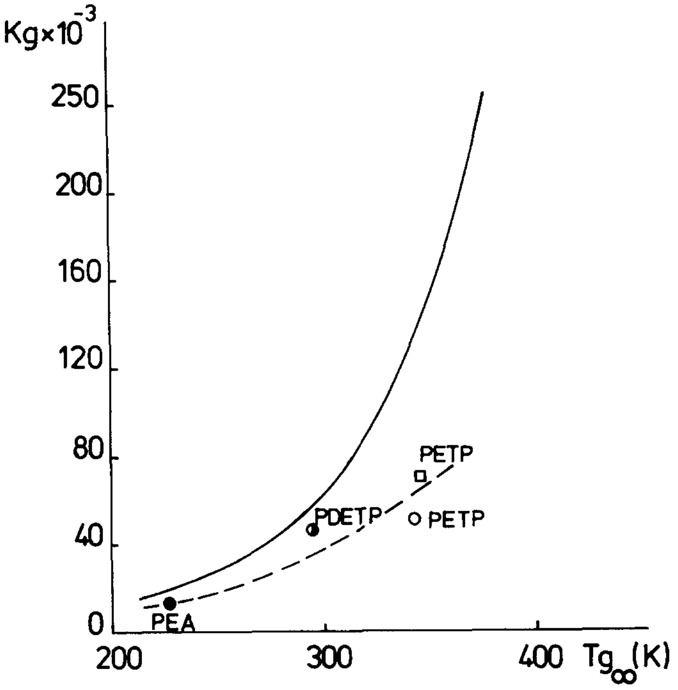

Figure 4. Correlation between Kg and Tg_{∞} calculated according to the Fox-Flory equation. Correlation suggested by Boyer (——) and experimental results for PEA (12), PDETP (13) and PETP for the whole Mn range (o) and for Mn > 10000 (□) only.

Table 2. Parameters of Fox-Flory equation.

Polymer	Tg (K)	Kg	Mn range	Standard error	Reference
PETP	342.4	51200	37100-4500	0.9	This paper
PETP	345.2	69500	37100-11750	0.7	This paper
PDETP	294.5	45700	22000-2500	1.2	From table I of ref.13.
PEA	227.5	13200	18000-1850	0.2	From table III of ref. 12.

terminal group of chain contributes to a θ excess free volume resulting the equation:

$$Tg = Tg_{\infty} - \frac{2\ \theta\ \rho N_A}{\Delta\alpha} \cdot \frac{1}{Mn} \qquad |2|$$

where $\Delta\alpha$ is the difference between the expansion coefficients below and above Tg, ρ is the polymer density and N_A the Avogadro's number. Comparing this equation with the Fox-Flory equation, on obtains:

$$Kg = \frac{2\ \theta\ \rho\ N_A}{\Delta\alpha} = \frac{2\ \theta\ N_A}{\Delta\beta} \qquad |3|$$

where $\Delta\beta = v\ \Delta\alpha = \left(\frac{\partial v}{\partial T}\right)_l - \left(\frac{\partial v}{\partial T}\right)_g$

A θ excess free volume of 12.3 $Å^3$ is obtained by applying the above equation to PETP with an experimental Kg of 51200 and taking the value of $\Delta\beta$ of 2.9×10^{-4} cm^3/g K suggested by Sharma et al. (20) for an amorphous PETP. The volume of structural unit, ν, can be evaluated by the expression $M_o/\ \rho N_A$. Taking ρ=1.335 g/cm^3 , corresponding to the non-oriented amorphous polymer (19), a value of $\nu = 238.8$ $Å^3$ and a ratio θ/ν of 0.05 is obtained. The latter value means that each chain end introduces as free volume about 5 per cent of the average volume per repeat unit.

Considering in the PETP the range of high molecular weights only, $Mn > 11750$ with Kg = 69500, we find $\theta = 33.5$ $Å^3$ and a ratio θ/ν of 0.14, also low and close to that of the poly(propylene oxide) (see table 2, reference 7).

This value is even smaller in PEA for which Onder et al. (12) have found a value of $\theta = 6$ $Å^3$ and a θ/ν ratio of 0.03, considering $\nu = 220$ $Å^3$ the volume of the structural unit. In this case, only a 3 per cent of the volume of repeat unit may be attributed to the free volume of the end of the chain.

The small variation of Tg with molecular weight in PETP, in our opinion, is due to the reduced contribution to the chain mobility of the end groups rather than to an excessive flexibility of the chain. The aliphatic part of the chain may contribute to its flexibility while the aromatic rings of the terephthalate group reduce their mobility, which is reflected in the moderately high value of Tg.

The dependence of Tg on the molecular weight can be also studied by the statistical mechanical theory of the undercooled liquids proposed by Gibbs and Di Marzio (16). This theory introduces a parameter related with the stiffness of the chain, the flex energy ε respect the difference of energy between rotational conformers. The relation between Tg and the chain length is given by the following equation:

$$\frac{x}{x-3}\left\{\frac{\ln v_o}{1-v_o} + \frac{1+v_o}{1-v_o}\ \ln\left[\frac{(x+1)(1-v_o)}{2\ v_o} + 1\right] + \frac{\ln 3(x+1)}{x}\right\} =$$

$$= \frac{2\ \beta \exp \beta}{1+2 \exp \beta} - \ln\ (1+2 \exp \beta\ ) \qquad |4|$$

with:

$$\beta = -\ \frac{\varepsilon}{k\ Tg} \qquad |5|$$

x being the number of atoms of the macromolecular chain, v_o the fraction of the free volume at Tg and ε the flex energy.

For PETP of the extreme molecular weights of 37100 (Tg = 342 K) and of 4500 (Tg = 331.3), the ε values of 1485 and 1480.6 cal/mol have been respectively obtained, assuming $v_o = 0.025$. Therefore, there is not a substancial difference between the flex energy in chains of different lengths (x = 1930 and 230 respectively), that is, ε is practically independent of x. In other polyesters as in the PEA (12) ε is a function of 1/x.

Assuming the value of ε of 1483 cal/mol we calculated Tg values which fit quite well with the experimental ones, as it can be seen in the figures 1 and 2.

This value of ε of PETP is intermediate between the one shown by some polymers with more flexible chain, such as polyolefins and polysiloxanes (ε between 600 and 800 cal/mol), and others polymers with stiffer chain, such as sodium and calcium phosphate copolymer (ε between 2500 and 3500 cal/mol).This comparison of ε values shows that the flexibility of the PETP chain cannot be as high as it appears taking only into account the low value of the parameter Kg of Fox-Flory equation.

In PEA, the ε value is 963 cal/mol for Mn = 1850 and 850 cal/mol for Mn = 18000. These values are similar to those observed in polymers with flexible chain like polyisobutylene (ε = 872 cal/mol). A larger flexibility of the chain is usual in this polymer which leads to a lower value of ε as well as a low value of Kg.

CONCLUSIONS

The little variation of the Tg with the molecular weight in PETP and, hence, the low value of the parameter Kg of Fox-Flory equation is understood considering the small contribution of the chain ends to the free volume; in fact, the free volume introduced by the chain ends is just a 5 % of the volume of the structural unit. On the other hand, the flexibility of the chain is not that corresponding to polymers with very flexible chain and low Kg, since the Tg has a moderately high value due to the presence of the aromatic ring in the polymeric chain.

The flex energy evaluated by the theory of Gibbs and Di Marzio shows that the PETP presents an intermediate flexibility between the polymers with a very flexible chain and those with stiff chain.

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