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THERMAL ANALYSIS AND MOLECULAR WEIGHT DEPENDENCE ON GLASS TRANSITION OF POLY(DITRIMETHYLENE TEREPHTHALATE)

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ABSTRACT

Eight fractions of poly(ditrimethylene terephthalate)(PTMTMT) were characterized by viscometry, osmometry and thermal analysis. The four fractions of higher molecular weight fitted a linear variation of the glass transition temperature (Tg) with the inverse of the molecular weight, and the other ones showed a non-linear behaviour. A value of the parameter b/a = 0.84 was obtained when the Somcynsky-Patterson equation was used, showing that PTMTMT is a relatively flexible polymer and slightly more rigid than the preceding member of the series, poly(diethylene terephthalate) (PDET). Moreover, in order to evaluate the dependence of Tg with molecular weight, the Gibbs-DiMarzio equation was applied, using $\epsilon = 1160$ cal mol^{-1} for reaching the best correlation This value also corresponds to flexible polymers.

INTRODUCTION

The flexibility of aromatic polyesters can be improved either by increasing the number of methylenic units of the glycol moiety or inserting heteroatoms, like ether groups, in it. The latter approach is used in the synthesis of PTMTMT, of which the structural unit is $-O-(CH_2)_3-O-(CH_2)_3-OCO-C_6H_4-CO-$.

The aim of this work is to get insight in the flexibility of this polymer through its thermal behaviour.For this purpose, the thermal properties of several PTMTMT fractions, characterized previously by viscometry and osmometry, are determined and discussed. Moreover, the relation between thermal properties (specially the glass transition temperature) and molecular weights of the PTMTMT fractions is studied in the context of the Somcynsky-Patterson and Gibbs-DiMarzio theories, leading to the evaluation of parameters related to the flexibility of the macro-

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molecule. The polymer studied is suitable for this type of investigations because its slow crystallization rate facilitates its formation in the amorphous state by quenching on ice from the melt.

EXPERIMENTAL

Ditrimethylene glycol was obtained by cleavage of oxetane with trimethylene glycol in the presence of sulphuric acid, using methylene chloride as solvent. The polyester PTMTMT was prepared by the melt phase procedure from ditrimethylene glycol and dimethyl terephthalate using tetraisopropyl titanate as catalyst. Eight fractions were obtained by fractionation of the polyester and characterized by viscometry and osmometry.

The glass transition temperature of the polyterephthalate fractions was determined by calorimety, using a Mettler-TA 3000 differential scanning calorimeter. The samples were encapsulated in aluminium pans, quenched from the melt into liquid nitrogen and heated at a rate of 10 °C min^{-1}. During the measurements, an empty pan was used as reference. The calorimeter was calibrated with high purity indium and tin. The Tg was taken to be the lowest temperature at which the base line of the thermogram has an inflexion point.

RESULTS AND DISCUSSION

Several relations have been proposed to predict the dependence of the glass transition temperature on the polymeric chain length. The most common one is the empirical linear equation

$$Tg = Tg_{\infty} - K\ Mn^{-1} \qquad |1|$$

The variation of Tg as a function of the inverse of the number-average molecular weight is plotted in Fig. 1. It can be seen that this dependence is linear over the range of high molecular weights (up or equal to 2.4×10^4). On the other hand, the low molecular weight samples show glass transition temperatures higher than the predicted by the straight line derived from the four fractions of high molecular weight, as it has also been found for other polymers (1).

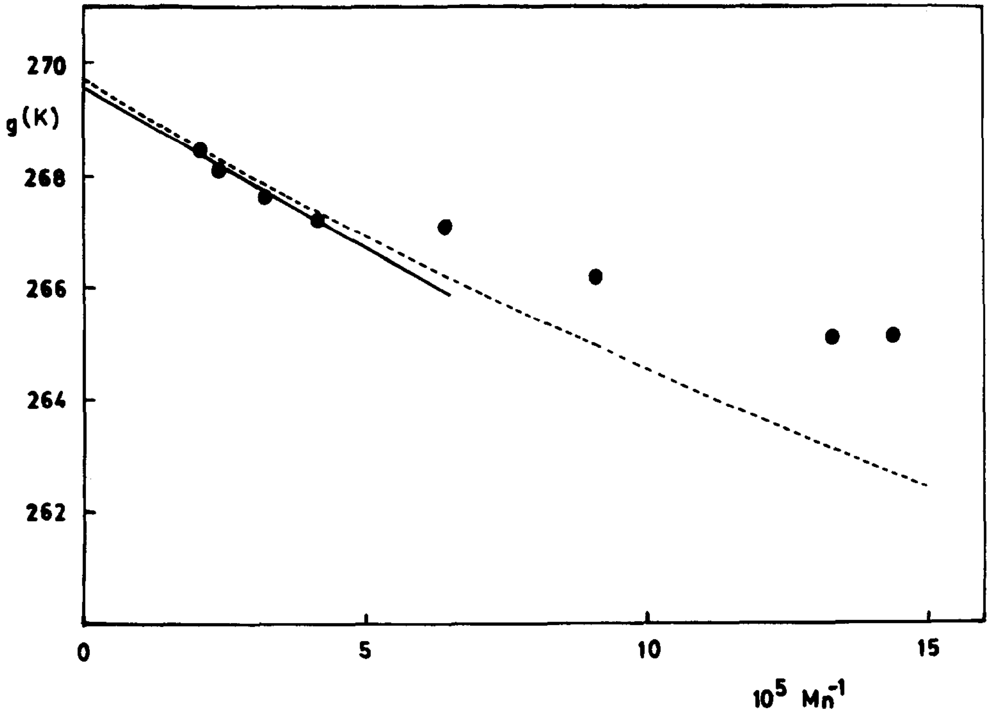

Fig. 1. Dependence of glass transition temperature on number-average molecular weight for poly(ditrimethylene terephthalate) fractions. ●, experimental points. —— and ---, lines derived from the Somcynsky-Patterson and Gibbs-DiMarzio theories, respectively.

Equations similar to |1| have also been derived, only differing in the physical meaning of the constant K, which depends on the assumptions concerning the nature of the factors governing the glass transition. Thus, Somcynsky and Patterson (2) developed a treatment as an extension of the Prigogine theorem of corresponding states, trying to explain the molecular weight dependence of the glass transition temperature in terms of the chain stiffness. Assuming that samples of different molecular weight are in corresponding states at their glass transition temperature, they obtained a value of K given by the expression

$$K = b\ M_0\ Tg\ a^{-1} \qquad |2|$$

where M_0 is the molecular weight of a chain segment, and (b/a) a quantity related to the chain flexibility.

The Somcynsky and Patterson treatment has been applied to our experimental data, and the results are also plotted in Fig. 1. The values obtained were $K = 5.96 \times 10^4$ mol K g^{-1} and $Tg_{\infty} = 269.6$ K. The calculations were carried out considering M_0 as the molecular weight of the repetitive unit of the polymer, resulting b/a = 0.84. This ratio decreases as a polymer chain becomes more flexible, and therefore it can be used as a measure of the chain flexibility (3). For a highly flexible polymer a value of b/a = 0.5 was estimated, and for rigid polymers like the vinyl ones, values of b/a higher than 2 are obtained. Accordingly, our results show that PTMTMT is a relatively flexible polymer. The PDET, a polymer which chemical structure is quite similar to the PTMTMT one, has a b/a value of 0.70 (4), showing that PDET is slightly more flexible than PTMTMT. The characteristic ratios of the same polymers also confirm this result (5).

As shown in Fig. 1 and commented above, the linear dependence ·Tg vs. Mn^{-1} is not satisfactory in the low molecular weight range. In some cases, the Gibbs-DiMarzio (6) treatment revealed as a useful method to reproduce the experimental data (7). This treatment has its origin in the Gibbs-DiMarzio theory of supercooled liquids, and assumes that a flexible chain, on cooling, may pass into an amorphous equilibrium state at a characteristic temperature T_2, related to Tg. The relationship derived for the variation of Tg with the chain length is given as a function of the flexion energy, ϵ.

Through iterative calculations for the fraction of the higest molecular weight, a value of $\epsilon = 1160$ cal mol^{-1} is reached. It can be seen in Fig. 1 that this treatment predicts correctly the Tg_{∞} for the polymer and shows good agreement with the experimental data when the molecular weight of the sample is higher than around 2×10^5. However, it cannot predict the depression of the Tg for molecular weights lower than that value.

Values of ϵ have been reported for several polymers, using the Gibbs-DiMarzio treatment (8). They are in the range between 600 cal mol^{-1} for highly flexible chains and 3600 cal mol^{-1} for the rigid ones. According to the result of this work (1160 cal mol^{-1}), PTMTMT can be considered a relatively flexible polymer.

CONCLUSIONS

We can conclude that both the Somcynsky-Patterson and Gibbs-DiMarzio treatments show a good correlation with the experimental data of PTMTMT in the high molecular weight range. However, they cannot predict the dependence of Tg on number-average molecular weight for the low molecular weight interval. The Gibbs-DiMarzio theory shows the best agreement in the full range of molecular weights.

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