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# Glass Transition Temperature-molecular Weight Relation for Poly(hexamethylene perchloroterephthalamide)

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## SUMMARY

In order to determine the Tg variation with the molecular weight, several fractions of poly(hexamethylene perchloroterephthalamide) were studied. The Tg-molecular weight relationship wasestablished to determine the $Tg^{\infty}$ and K values of Fox-Flory relationship.

The glass transition temperature depends strongly on the molecular weight, especially at lower molecular weights due to the free volume around the chain ends.

Fox-Flory (1) deduced the expression

$$Tg = Tg^{\infty} - K\,M^{-1} \qquad (1)$$

where Tg is the glass transition temperature of the molecular weight M, $Tg^{\infty}$ the glass transition temperature of a infinite molecular weight polymer and K a constant.

This investigation was undertaken to describe the molecular weight effect on the glass transition temperature of a polychlorinated polyamide, synthetized

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TABLE I

Data of glass transition temperatures, molecular weights and intrinsic viscosities for the different polymer fractions.

| Fraction | Tg$^a$ | $[\eta]^{b,c}$ | $M_V \cdot 10^{-3}$ |
|---|---|---|---|
| I | 290 | 0,68 | 20,19 |
| II | 284 | 0,55 | 15,77 |
| III | 280 | 0,50 | 15,60 |
| IV | 278 | 0,44 | 12,16 |
| V | 270 | 0,34 | 9,10 |
| VI | 211 | 0,11 | 2,43 |

a: °C; b: in $H_2SO_4$ at 25°C; c: dl $g^{-1}$

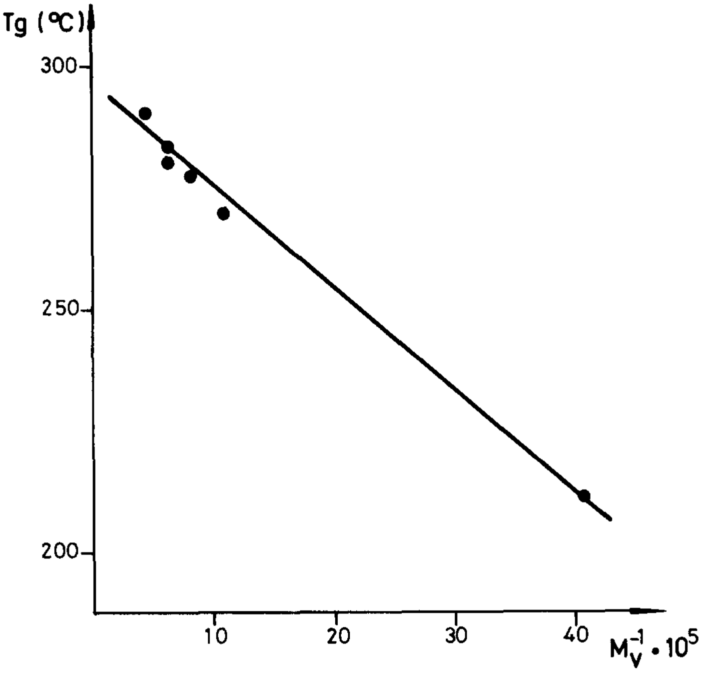

Figure 1: Plot of Tg versus $M_V^{-1}$ for the fractions of the polyamide.

by Díaz et al. (2). Poly(hexamethylene perchloroterephthalamide) was synthetized by interfacial condensation of perchloroterephthaloyldichloride and hexamethylenediamine. It was fractionated and the intrinsic viscosities and the glass transition temperatures of the fractions were determined. The fractions were obtained by fractionated precipitation with m-cresol/cyclohexane as the solvent-precipitant pair. The viscometric measurements were carried out with the dilution viscosimeter of the Desreux-Bischoff (3) type. The glass transition temperatures were measured with a Differential Scanning Calorimeter Perkin-Elmer DSC-1B, with a heating rate of 16°C/min under nitrogen flow.

The molecular weights of the fractions were calculated from the viscosimetric measurements applying the Mark-Houwink relationship, using values of a and K, 0,86 and $1,35 \cdot 10^{-4}$, respectively, as reported in literature for polyamides (2)(4).

Table I gives the values of $[\eta]$, Tg and $M_V$ for the different polymer fractions. Figure 1 shows the dependence of Tg on the reciprocal of molecular weight. A linear relationship between Tg and $M_V^{-1}$ has been found, with $Tg^{\infty}$ and K 296°C and $2,08 \cdot 10^5$, respectively.

The high value of $Tg^{\infty}$ for the polychlorinated polyamide is in agreement with the values given for other polyamides derived from the same monomer and other diamines (Díaz et al. 2) and for others polyamides synthetized by Escobar et al. (5) from perchloro-4,4'-dichloroformylbiphenyl and several diamines. The great volume of the aromatic ring linked to four chlorine atoms apparently increases the polymer rigidity and therefore the Tg value.

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