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EFFECT OF THE SIDE CHAIN STRUCTURE ON THE GLASS TRANSITION TEMPERATURE. PART 3. MOLECULAR WEIGHT DEPENDENCE OF T_g IN SOME POLY(THIOCARBONATES)

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ABSTRACT

Different $T_g - \overline{M}_n$ (number-average molecular weight) relationships for poly(oxythiocarbonyloxy-1,4-phenylene-2,2-propyl-1,4-phenylene) (PMMT), poly(oxythiocarbonyloxy-1,4-phenylene-2,2-butyl-1,4-phenylene) (PMET), poly(oxythiocarbonyloxy-1,4-phenylene-(4-methyl)-2,2-pentyl-1,4-phenylene) (PMiBT), and poly(oxythiocarbonyloxy-1,4-phenylene-(methyl)phenylmethylene-1,4-phenylene) (PMPhT) have been established in order to obtain the glass transition temperature in the limit of high molecular weight $T_{g\infty}$. Non linear dependence between T_g and $\overline{M}_n^{-1}$ is found, for PMMT and PMPhT, but the relationship between T_g and log M shows a linear dependence. The variations of the values of $T_{g\infty}$ and the values of the conformational parameter σ with the polymer structure are compared for the different polymers.

INTRODUCTION

In previous papers [1,2] we have reported the effect of the side chain structure on the glass transition temperature in a family of poly(thiocarbonates) [1] and in some poly(*o*-alkylphenyl methacrylates) [2]. Particularly interesting are the different relationships dealing with the variation of T_g with the chain length [2–5]. In fact, several relationships have been developed to describe the variation of T_g with the number-average molecular weight $\overline{M}_n$ [2,4,5]. The most widely used of these equations is that of Flory and Fox [3] in which a linear relation between T_g and the inverse of $\overline{M}_n$ is predicted. However, it has been demonstrated by several authors [2,4–7] that this equation deviates from linearity, mainly at high molecular weights. Fedors [4,8] has proposed an equation similar in form to that of Flory and Fox [3] which can be used to represent T_g and $\overline{M}_n$ data over the entire range of molecular weights. Ueberreiter and Kaning have found a simple equation which relates T_g^{-1} and $\overline{M}_n^{-1}$ in a linear form [7]. In a previous paper [2] we

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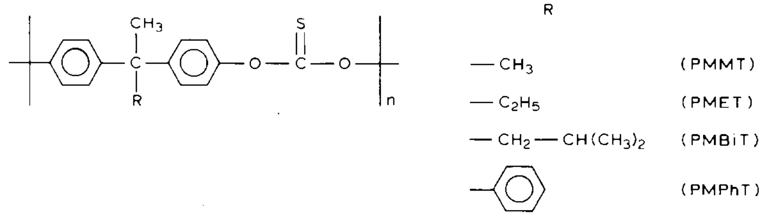
have reported a linear representation between T_g and the logarithm of the degree of polymerization. Similar relationships were found for several poly(styrene) samples [9], but in this case the variation of T_g with the degree of polymerization seems to depend on three distinct linear relationships.

In this work we report the variation of T_g with number-average molecular weight for a family of poly(thiocarbonates), i.e. poly(oxythiocarbonyloxy-1,4-phenylene-2,2-propyl-1,4-phenylene) (PMMT), poly(oxythiocarbonyloxy-1,4-phenylene-2,2-butyl-1,4-phenylene) (PMET), poly(oxythiocarbonyloxy-1,4-phenylene-(4-methyl)-2,2-pentyl-1,4-phenylene) (PMiBT), and poly(oxythiocarbonyloxy-1,4-phenylene(methyl)phenylmethylene-1,4-phenylene) (PMPhT) (see structures), and we describe this variation by using the different equations obtained from the literature, in order to check the validity of these relationships in this kind of polymer.



EXPERIMENTAL

Monomer and polymer preparation

Diphenols were obtained by condensation of phenol with the corresponding aldehyde or ketone according to the procedure of McGreal et al. [10].

Poly(thiocarbonates) were synthesized by phase transfer catalysis from diphenols and thiophosgene using several quaternary ammonium and phosphonium salts in dichloromethane as solvent. The synthesis and characterization of these polymers have been described in detail in our previous papers [11,12].

Molecular weight determination

The weight average molecular weight ($\overline{M}_w$) of fractions was determined by size exclusion chromatography (SEC), using a Perkin-Elmer high performance liquid chromatograph (HPLC) equipped with a 6000 psi pump, a Perkin-Elmer differential refractometer model LC-25, and an injector of 175 μl. Three Waters Associates Ultra Styragel™ columns (10^3, 10^4 and 10^5 Å) in series were used. Samples were eluted with THF and the flow rate was 1.0

ml/min. The columns were first calibrated with standard poly(styrene) samples of narrow molecular weight distribution. It has been shown [12–14] that the calibration curve obtained from such poly(styrene) fractions is adequately precise for determining the molecular weight of bisphenol-A-poly(carbonate), for $\overline{M}_w > 5{,}000$, and for poly(thiocarbonates). For samples of very low molecular weight a Shodex A-803 column was used.

A Hewlett-Packard high speed membrane osmometer model 502 was used for osmotic determination in chlorobenzene solutions at 300 K. The experimental values are in good agreement with those given by the classical osmotic relationships for determining number-average molecular weight $\overline{M}_n$.

A Knauer digital vapour pressure osmometer model 11.00 equipped with an universal thermistor probe was used for determination of number average molecular weight of samples of low molecular weight.

Differential scanning calorimetry (DSC)

The glass transition temperature (T_g) of polymer samples was measured using a Perkin-Elmer Model DSC-1B differential scanning calorimeter. Polymer samples were dried under reduced pressure in a vacuum oven prior to measurement. Samples (10–15 mg) were weighed into the DSC aluminium pans. Dry nitrogen was used as a purge gas and thermograms were measured between 300 and 500 K at scan rates of 16 K min^{-1}. Regular calibration of the instrument was carried out using metal standard.

Before measuring the glass transition all samples were first heated to the upper temperature limit (500 K) and quenched to the starting temperature in order to minimize differences in thermal history. The glass transition was located as baseline shift on the thermogram, and the value of T_g was estimated from the point of intersection of the sloping portion of the curve resulting from the baseline shift.

RESULTS AND DISCUSSION

Table 1 summarizes the T_g values for fractions of different number-average molecular weights $\overline{M}_n$ (or degree of polymerization P) of PMMT, PMET, PMiBT and PMPhT. The polydispersity indexes of the fractions $\overline{M}_w/\overline{M}_n$ are in the range 1.1–1.3 for the first three members of the series and 2.0–2.1 for the PMPhT.

One of the most important factors influencing T_g is considered to be the bulkiness of the pendant groups which impose steric restrictions on the rotation of the main chain: the T_g value in each group should increase as the total volume of the side chain increases. Exceptions arise when some degree of flexibility is introduced into the side chain of the polymer, as was shown in a previous paper [1] for this family of polymers.

TABLE 1

Glass transition temperature T_g, number-average molecular weight $\overline{M}_n$ and degree of polymerization P for different fractions of PMMT, PMET, PMiBT and PMPhT

	Fractions								
	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	F_9
PMMT ($T_{g\infty}$ = 441)									
$\overline{M}_n \times 10^{-4}$	15.60	11.40	5.40	4.55	3.67	3.03	2.42	1.82	1.67
$P \times 10^{-2}$	5.80	4.20	2.00	1.69	1.36	1.12	0.90	0.67	0.62
T_g (K)	435	431	427	424	418	418	418	411	409
PMET ($T_{g\infty}$ = 400)									
$\overline{M}_n \times 10^{-4}$	1.78	1.41	1.00	0.63	0.45	0.40			
$P \times 10^{-2}$	0.63	0.50	0.35	0.22	0.16	0.14			
T_g (K)	393	392	389	383	376	374			
PMiBT ($T_{g\infty}$ = 406)									
$\overline{M}_n \times 10^{-4}$	1.58	1.26	0.89	0.63	0.50	0.40			
$P \times 10^{-2}$	0.53	0.43	0.31	0.21	0.17	0.14			
T_g (K)	400	399	397	393	384	380			
PMPhT ($T_{g\infty}$ = 488)									
$\overline{M}_n \times 10^{-4}$	7.1	4.5	4.2	1.3	0.7				
$P \times 10^{-2}$	2.24	1.42	1.33	0.41	0.22				
T_g (K)	480	467	464	437	422				

The main aspect to take into account when comparing glass transition temperatures of different polymers is to ensure that polymers have molecular weights above which T_g becomes independent of the molecular weight and to have samples with similar tacticities. For this reason, in most cases it is necessary to obtain T_g values at infinitely large molecular weight, i.e. $T_{g\infty}$.

Figure 1 shows the variation of T_g with the inverse of the number average molecular weight $\overline{M}_n^{-1}$ for PMMT, PMET, PMiBT and PMPhT, in order to determine $T_{g\infty}$, according to the Flory and Fox [3] equation. A linear relationship was found for PMET and PMiBT but not for PMMT and PMPhT. Although the polymolecularity index of PMPhT is high, we think that the deviation from linearity is not due to the polydispersity, because we obtained well-defined and reproducible glass transitions. It is very difficult to obtain $T_{g\infty}$ in the case of PMMT and PMPhT; we could only obtain $T_{g\infty}$ by extrapolation of the curve or by taking into account only high molecular weight, and therefore considering the function as a straight line. This behaviour has been reported previously by Fedors [4] and recently by Gargallo et al. [2] in different kinds of polymers. However, in the case of this family of poly(thiocarbonates) the fractions of PMMT and PMPhT have higher molecular weight than those of PMET and PMiBT which could explain the different behaviour according to the Fox and Flory equation [3].

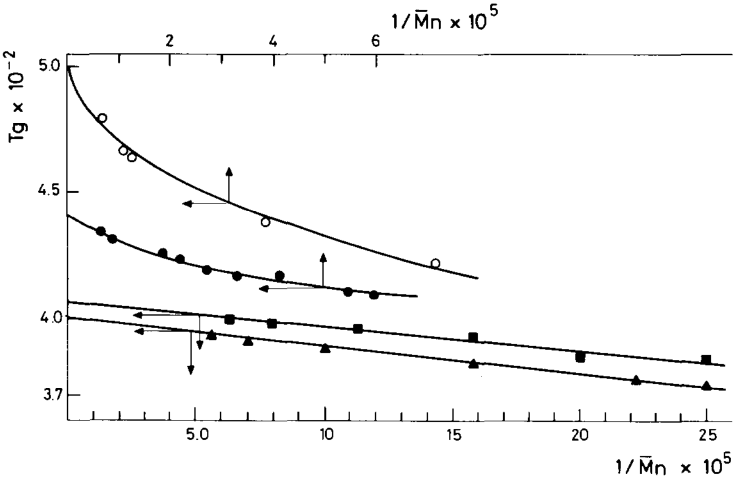


Fig. 1. Variation of T_g with the inverse of number average molecular weight ($\bar{M}_n^{-1}$) for PMMT (●), PMET (▲), PMiBT (■), and PMPhT (○).

The Fox and Flory [3] equation deviates from a straight line for high molecular weight [2,4]. Unfortunately it was very difficult to obtain samples of PMET and PMiBT of higher molecular weights. Table 2 summarizes the $T_{g\infty}$ values obtained from two different T_g–$\bar{M}_n$ relationships and determined by extrapolation of the straight lines or from the curves, considering only high molecular weights. These results are in good agreement with that of

TABLE 2

Values of infinite glass transition temperature $T_{g\infty}$ (determined by using equations given in refs. 3, 4 and 7, and extrapolating the curve or straight line considering only high molecular weights) rigidity factor σ, characteristic ratio C_∞, and molar volume of the side groups taken from ref. 15

Polymer	$T_{g\infty}$ (K)				V [e] (cm^3 mol^{-1})	σ [f]	C_∞ [f]
	a	b	c	d			
PMMT	441	439	439	439	25.9	1.25	3.84
PMET	400	–	402	–	48.1	1.27	4.08
PMiBT	406	–	410	–	92.5	1.48	5.48
PMPhT	500	488	493	500	92.3	1.43	4.98

[a] From $T_g = T_{g\infty} - K/M$ [3] by direct extrapolation of the curve or straight line (Fig. 1).

[b] From $T_g = T_{g\infty} - K/M$ [3] by extrapolation of the straight line considering only high molecular weight (Fig. 1).

[c] From $1/T_g = 1/T_g + C/P$ [7] by direct extrapolation of the curve or straight line (Fig. 2).

[d] From $1/T_g = 1/T_{g\infty} + C/P$ [7] by extrapolation of the straight line considering only high molecular weight.

[e] From ref. 15.

[f] From ref. 14.

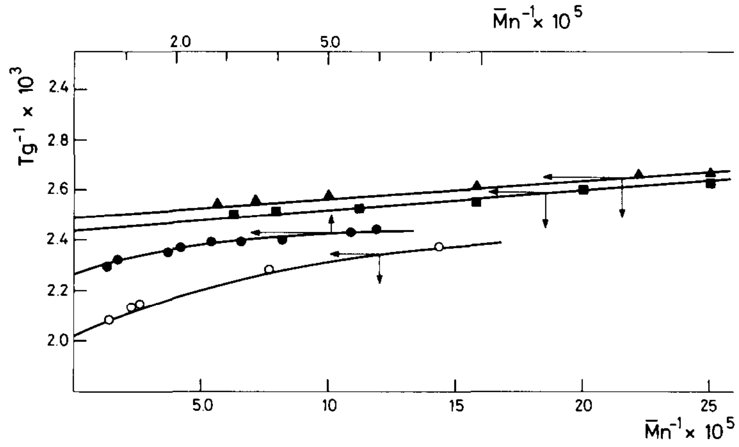


Fig. 2. Variation of T_g with the inverse of number average molecular weight ($\bar{M}_n^{-1}$) for PMMT (●), PMET (▲), PMiBT (■), and PMPhT (○).

Fedors [4] for poly(styrene) in the sense that a single equation as that proposed by Fox and Flory [3] does not relate the variation of T_g with the number average molecular weight over the entire range of values of $\bar{M}_n$, i.e. including high and low molecular weights. Therefore, it is necessary to investigate other equations in order to obtain $T_{g\infty}$. In Figure 2 we have plotted the variation of T_g^{-1} as a function of $\bar{M}_n^{-1}$ according to the equation proposed by Ueberreiter and Kaning [7]. As can be seen in this figure, PMET and PMiBT conform to this equation, but again PMMT and PMPhT do not show linear behaviour. As in the case of Fig. 1, we could attribute this deviation from linearity to the differences in the range of molecular weight considered. Furthermore the differences between the values obtained by extrapolation from the different methods of obtaining $T_{g\infty}$ are very slight. Because of this we can consider that the values of $T_{g\infty}$ so obtained are valid.

The $T_{g\infty}$ values obtained by using the Fox and Flory [3], Fedors [4] and the Ueberreiter and Kaning [7] equations are similar for each one of the systems here studied (see Table 2). In Table 2 we also summarize the rigidity factor σ, the characteristic ratio C_∞, and the molar volume of the side chain taken from ref. 15 for the different polymers. It is interesting to note that the rigidity factor σ and the characteristic ratio C_∞ increase as the volume of the side chain increases in this family of polymers [12,14], but values of $T_{g\infty}$ do not follow the same trend. This behaviour can be explained in terms of the differences introduced due to the flexibility of the alkyl side chain. There is a kind of competition between the increase of T_g due to the increment of the molar volume or rigidity of the side groups (and size of the side groups) and the reduction due to the flexibility introduced by the spacer groups $-CH_2-$. In fact, polymers containing one methylene group in their lateral chains have lower T_g values than their immediate analogues [2].

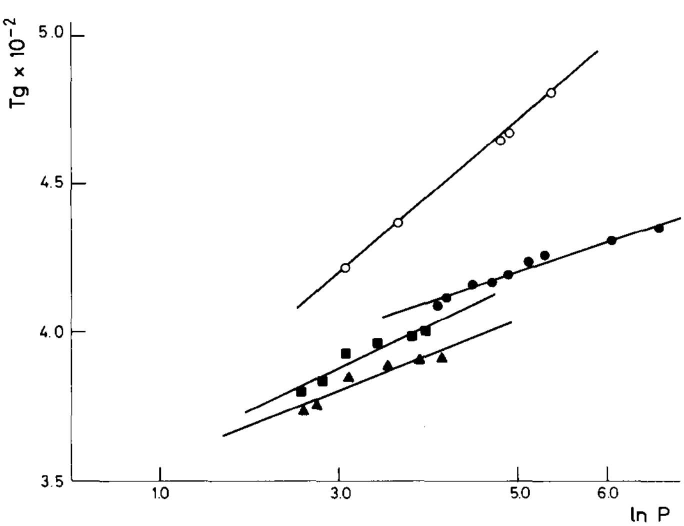


Fig. 3. Variation of T_g with ln P for PMMT (●), PMET (▲), PMiBT (■) and PMPhT (○) according to eqn. (1).

Figure 3 shows the variation of T_g with the logarithm of the degree of polymerization P for the different fractions of the polymers studied. As can be seen, good straight lines are obtained. Similar results have been found in poly(styrene) [9] and poly(alkylphenyl methacrylates) [2]. Although in the case of the former, the variation of T_g with the degree of polymerization depends on three distinct linear regimes [9]. The behaviour shown in Fig. 3 agrees with an equation of the form

$$T_g = T_{g(0)} + k \ln P \tag{1}$$

as reported by Gargallo et al. [2], where $T_{g(0)}$ is a temperature characteristic of the monomer unit [2] and k is a constant which depends on the polymer structure and is related to the rigidity of the polymer chain. According to our results and those of Claudy et al. [9], this relationship seems to be general. For this reason it would be interesting to investigate this behaviour with a wide family of polymers.

On the other hand, according to Fox and Flory [3] the relationship between T_g and M (or P), for poly(styrene) can be expressed as

$$T_g = T_{g\infty} \exp(-b_T/5M_0P) \tag{2}$$

where b_T is a parameter which is related to E_T, the apparent activation energy for viscous flow; M_0 is the molecular weight of the monomer unit and P the degree of polymerization. According to eqn. (2) a plot of ln T_g against P^{-1} should give b_T and $T_{g\infty}$. Figure 4 shows these plots for PMMT,

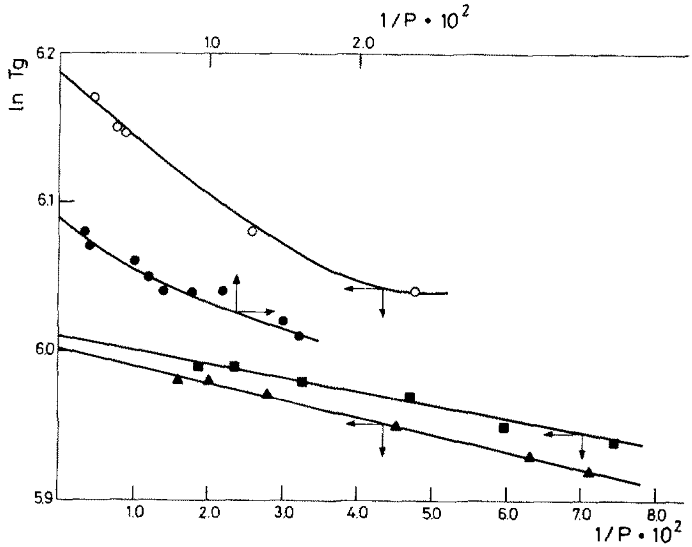


Fig. 4. Variation of ln T_g with $1/P$ for PMMT (●), PMET (▲), PMiBT (■) and PHPhT (○) according to eqn. (2).

PMET, PMiBT and PMPhT. As in the case of the other relationships used here, we found a linear relationship for PMET and PMiBT.

Table 3 summarizes the values of b_T and $T_{g\infty}$ obtained from this relationship. As can be seen, the values of $T_{g\infty}$ so obtained are in good agreement with those of Table 2.

The values of b_T are lower than those previously reported [2] for poly(methacrylates). These results confirm the general behaviour found in solution for poly(thiocarbonates) [14], which are more flexible than poly(methacrylates).

TABLE 3

Values of $T_{g(0)}$, k, b_T and $T_{g(\infty)}$ for PMMT, PMET, PMiBT and PMPhT obtained from eqns. (1) and (2)

Polymer	$T_{g(0)}$ [a] (K)	k [b]	b_T [c] (kcal/mol$^-$)	$T_{g\infty}$ [d] (K)
PMMT	370	10.0	5.00	441
PMET	346	11.5	1.70	404
PMiBT	346	14.0	1.33	407
PMPhT	343	25.5	1.26	498

[a] Obtained from the extrapolation to $P = 1$.
[b] Obtained from the slope of Fig. 3.
[c] Obtained from the slope of Fig. 4.
[d] Obtained from the extrapolation to $P \to \infty$ in Fig. 4.

CONCLUSION

From this study we can conclude that the various relationships used for determining the glass transition temperature at infinite molecular weight $T_{g\infty}$ give similar results, although for PMMT and PMPhT, we do not obtain straight lines according to the relations of Fox and Flory [3] and Ueberreiter and Kaning [7]. The values of $T_{g\infty}$ obtained by extrapolation of the curves are similar to $T_{g\infty}$ values obtained by extrapolating the straight lines considering only high molecular weights. All systems studied here show linear behaviour when T_g is plotted against ln P; this seems to be a general relationship when comparing these results with those for other polymers previously reported [2,9].

Finally, the variation of ln T_g with $1/P$ gives $T_{g\infty}$ values in good agreement with those obtained from the other equations, although this is a relation reported only for poly(styrene) [3].

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