Thermochimica Acta, 146 (1989) 137–147
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECT OF THE SIDE CHAIN STRUCTURE ON THE GLASS TRANSITION TEMPERATURE. PART 4. MOLECULAR WEIGHT DEPENDENCE OF T_g IN CHALCOGENIDES CONTAINING POLY(METHACRYLATES)

M.I. MUÑOZ, L. GARGALLO and D. RADIC *

Laboratorio de Química Física Molecular, Facultad de Química (502),
Pontificia Universidad Católica de Chile, Casilla 6177, Santiago (Chile)

(Received 28 October 1988)

ABSTRACT

Glass transition temperature T_g has been measured by DSC for several fractions of poly(benzylmethacrylate) (PBzM), poly(2-thienylmethyl methacrylate) (PTiM) and poly(2-selenolylmethyl methacrylate) (PSeM) and for one fraction of poly(2-furfurylmethyl methacrylate) (PFM) and poly(tetrahydrofurfurylmethyl methacrylate) (PHFM). The effect of the nature of the side group on T_g is discussed. Various relationships between number average molecular weight M_n and T_g have been established. Linear relationships between T_g and ln P (P = degree of polymerization) have been obtained for some of the systems studied here.

INTRODUCTION

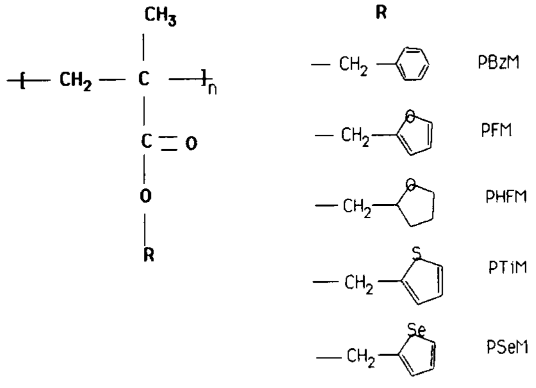
The glass transition temperature T_g is important in the characterization of polymers, as it can be altered in various ways [1]. Thus, in vinyl polymers the introduction of different side groups, flexible chains, bulky groups, samples with different tacticities, polarities or molecular weights, etc. produces noticeable effects on T_g [2–7]. Several empirical relationships have been developed to describe the dependence of T_g on molecular weight in order to obtain the value of $T_{g(\infty)}$, i.e. the value of T_g for samples of sufficiently high molecular weight where T_g becomes independent of the molecular weight. Linear relationships between T_g and the logarithm of the degree of polymerization P have also been reported recently [7,8].

Recent work in our laboratory has focused on the preparation, solid state and solution properties of poly(methacrylates) with aromatic rings of different aromaticity in the pendant ester group [9–12]. Furan, thiophene,

---

* Author to whom correspondence should be addressed.

0040-6031/89/$03.50



Scheme 1

selenophene and tellurophene form a very interesting series of four stable aromatic ring compounds which differ in the nature of the hetero atom [13]. The nature of the side group has been found to have a marked influence on chain rigidity σ [9–12]. This factor should also be reflected in T_g values for the polymers, since the rigidity of the polymer chain should have an important effect on the cooperative motions contributing to the glass transition temperature.

In this paper we report on the glass transition temperatures of fractions of different molecular weight of poly(benzyl methacrylate) (PBzM), poly(2-thienylmethyl methacrylate) (PTiM) and poly(2-selenolyl methyl methacrylate) (PSeM), and one fraction of poly(2-furfurylmethyl methacrylate) (PFM) and poly(tetrahydrofurfurylmethyl methacrylate) (PHFM). In order to compare the real T_g values for this family of poly(methacrylates), various T_g–M_n relationships were tested to obtain the glass transition temperature at infinite molecular weight $T_{g(\infty)}$. The effects of the nature of the heteroatom and of chain rigidity on T_g for the first three members of the series were then analysed.

EXPERIMENTAL

Monomer and polymer preparation

Methods for monomer and polymer preparation and characterization were as previously reported [9–11]. Polymerizations were achieved in similar conditions, i.e. in benzene solution under vacuum using AIBN as initiator at 323 K, in order to ensure similar tacticities.

Polymer characterization

The polymers were fractionated by fractional precipitation at 298 K, using benzene–methanol as solvent–precipitant pair.

The weight average molecular weight M_w and the polymolecularity index M_w/M_n were determined by size exlusion chromatography (SEC) using a Perkin–Elmer high performance liquid chromatograph equipped with a 6000 psi (0.84 Pa) pump, a differential refractometer LC-25 and a 175 μl injector. Five columns (three Waters Associates UltraStyragel (10^3, 10^4 and 10^5 Å) and two Shodex 805/S and 803/S) were used in series. Samples were eluted with THF. The apparatus was calibrated using polystyrene samples of narrow molecular weight distribution, characterized by light-scattering measurements. The flow rate was 1 ml min^{-1} and the volume of the injected polymer solution was always 5 μl. A universal calibration curve was used for the treatment of the data. Analysis of the elution data was performed according to the Rabek treatment [14]. The number average molecular weight M_n was determined in chlorobenzene at 333 ± 0.001 K by membrane osmometry in a Hewlett Packard high speed membrane osmometer (Model 502). A Knauer VPO osmometer (Model 11) equipped with a universal thermistor probe was used for fractions of low molecular weight.

Differential scanning calorimetry

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

Before measurement of 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 a baseline shift on the thermogram and' T_g was estimated from the point of intersection of the sloping portion of the curve resulting from the baseline shift.

RESULTS AND DISCUSSION

DSC measurement were performed for several fractions of PBzM, PTiM and PSeM, in order to determine the relations between T_g and M_n for these polymers. The dependence of T_g on M_n for the three polymers is shown in Fig. 1, and the values of T_g for fractions of different molecular weight (or

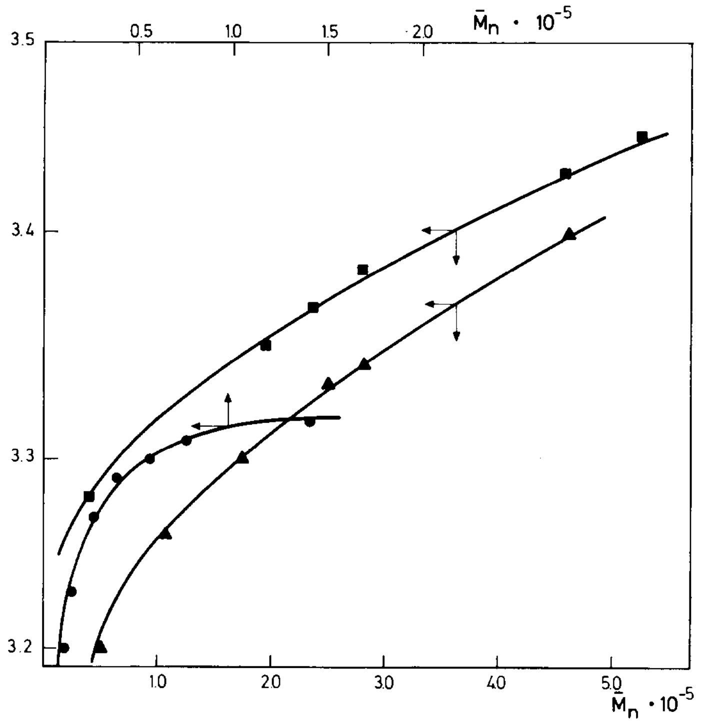


Fig. 1. Variation of T_g with number average molecular weight M_n for PBzM (▲), PTiM (■) and PSeM (●).

degree of polymerization P) are summarized in Table 1. As can be seen in Fig. 1, all three systems show a regular behaviour in the sense that T_g increases with increasing molecular weight. The range of molecular weights covered by our samples of PSeM is lower than that for PBzM and PTiM (see Table 1), so determination of $T_{g(\infty)}$ is more difficult, but the variation of T_g with M_n for PSeM reachs the asymptotic value very early (see Fig. 1) and therefore this can be related to $T_{g(\infty)}$.

Figure 2 shows the variation of T_g with M_n^{-1}, and Fig. 3 the variation of T_g^{-1} vs. M_n^{-1} according to the classical relations of Flory–Fox and Ueberreiter and Kaning, respectively, given by the known relationships [14,15]

$$T_g = T_{g(\infty)} - K/M_n \qquad (1)$$

and

$$1/T_g = 1/T_{g(\infty)} + C/M_n \qquad (2)$$

where K and C are constants for each system, dependent on the polymer structure.

These relationships could be used to determine $T_{g(\infty)}$ values for the various polymer samples. Although representations such as those in Figs. 2 and 3 might be expected to be linear, deviations from linearity have been

TABLE 1

Glass transition temperatures T_g, number average molecular weights M_n, polydispersity indices M_w/M_n and degree of polymerization P for different fractions of PBzM, PTiM and PSeM

	Fractions						
	F1	F2	F3	F4	F5	F6	F7
PBzM							
$M_n \times 10^{-5}$	4.61	2.82	2.50	1.73	1.05	0.53	-
M_w/M_n	1.42	1.32	1.33	1.32	1.26	1.41	-
$P \times 10^{-3}$	2.63	1.61	1.43	0.98	0.60	0.30	-
T_g (K)	340	335	334	330	326	320	-
PTiM							
$M_n \times 10^{-5}$	5.25	4.57	2.81	2.36	1.96	0.40	-
M_w/M_n	1.29	1.20	1.21	1.25	1.08	1.20	-
$P \times 10^{-3}$	2.86	2.50	1.54	1.30	1.08	0.22	-
T_g (K)	347	345	340	338	336	328	-
PSeM							
$M_n \times 10^{-5}$	1.41	0.75	0.56	0.38	0.25	0.15	0.11
M_w/M_n	1.33	1.33	1.33	1.26	1.28	1.30	1.28
$P \times 10^{-3}$	0.62	0.33	0.24	0.17	0.11	0.07	0.05
T_g (K)	332	331	330	329	327	323	320

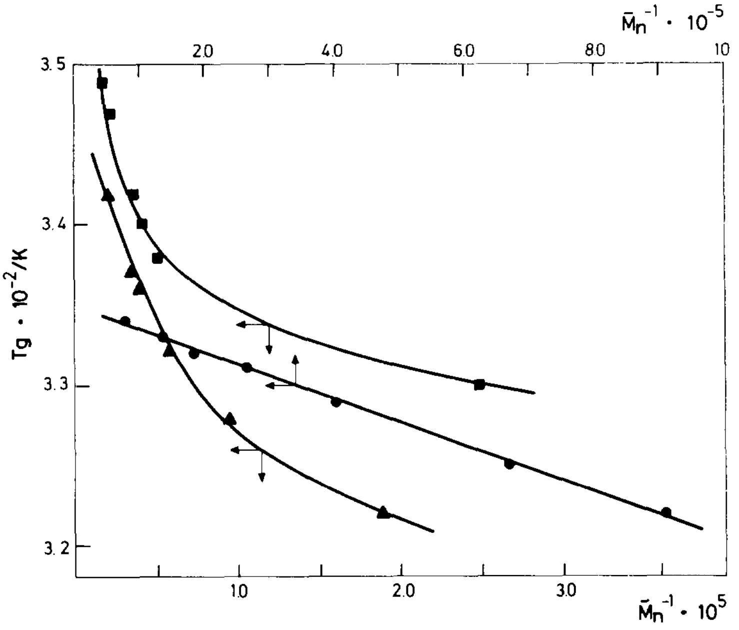


Fig. 2. Variation of T_g with the inverse of M_n for PBzM (▲), PTiM (■) and PSeM (●).

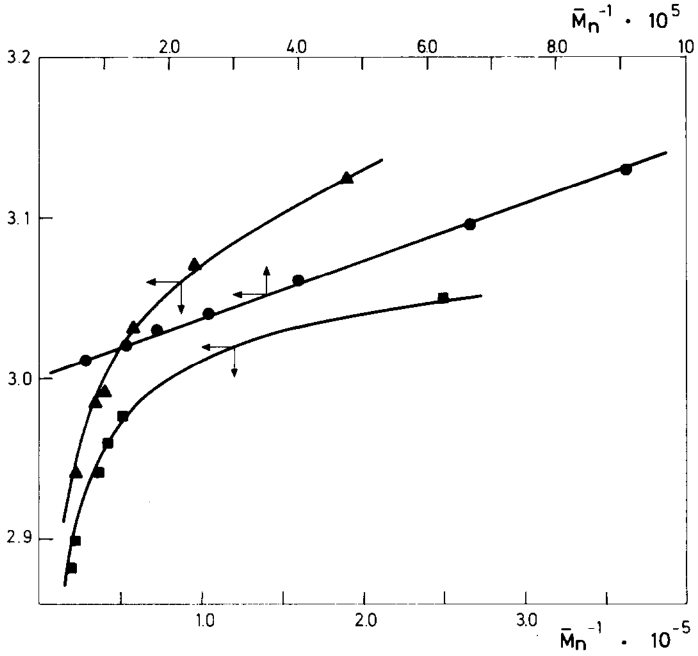


Fig. 3. Variation of T_g^{-1} with M_n^{-1} for PBzM (▲), PTiM (■) and PSeM (●).

shown to arise, depending on the range of molecular weights considered [7,8]. For instance, it is very common to find that both relationships deviate from linearity at very high molecular weights [7,8,16]. Several studies in this area show linear relationships [2,7,8,17,18], but this could be due to the fact that the range of molecular weights covered by these systems do not represent a sufficiently extended range of M_n to allow detection of deviation from linearity.

Figures 2 and 3 show this behaviour. Thus, in the case of PSeM, for which only a narrow range of molecular weights is covered, we find linear relationships; but with PBzM and PTiM, for which a wider molecular weight range is covered, we can see an exponential increase of T_g with increasing molecular weight (see Fig. 2) and a decrease of T_g (see Fig. 3). Unfortunately it was impossible to obtain higher molecular weights for PSeM and lower molecular weights for PBzM and PTiM in order to represent T_g–M_n data over the entire range of M_n and allow a clearer demonstration of this trend, which seems to be general for systems composed of vinyl or condensation polymers [7,8]. Therefore when deviations from linearity take place, $T_{g(\infty)}$ cannot be determined directly by extrapolation from straight lines to infinite molecular weight, but only by extrapolation of the curve or by taking into account only high molecular weights and extrapolating the resulting straight lines. These last two methods for the determination of $T_{g(\infty)}$ have been demonstrated in previous papers [7,8]. Table 2 summarizes

TABLE 2

Values for infinite glass transition temperature $T_{g(\infty)}$ determined using eqns. (1) and (2) and by extrapolation of the curve or straight line considering only high molecular weights, rigidity factor σ, molar volume of the aromatic ring V, and aromaticity A of the pendant group

Polymer	$T_{g(\infty)}$ (K)				σ	V [e]	A [e]
	a	b	c	d		(cm^3)	
PBzM	345	348	346	346	2.32	88.8	13.93
PTiM	353	355	353	356	2.41	78.9	11.56
PSeM	333	–	333	–	2.90	85.2	10.44

[a] From eqn. (1), considering only high molecular weights.
[b] From eqn. (1) and extrapolating the curve.
[c] From eqn. (2), considering only high molecular weights.
[d] From eqn. (2) and extrapolating the curve.
[e] Aromaticity obtained from ref. 13 and determined by NMR measurements.

the $T_{g(\infty)}$ values obtained using eqns. (1) and (2) and both these extrapolation methods. As can be seen, no significant differences obtain between the different systems. Table 2 also summarizes values of the rigidity factor σ for the polymers, taken from the literature [9,11].

The values of $T_{g(\infty)}$ for the various polymer samples decrease in the order PTiM > PBzM > PSeM. A higher value of $T_{g(\infty)}$ might have been expected for PSeM given the high value of σ for this polymer, but this is an abnormally high value of σ [11]. On the other hand, Table 2 indicates that there is no correlation between $T_{g(\infty)}$ and σ or molar volume V or aromaticity A. It could be that PBzM is not comparable with the other polymers from the thermal point of view, despite its being the first aromatic member of the series. For this reason we determined T_g for a sample of poly(furfurylmethyl methacrylate) (PFM) and found this to be higher than that for PTiM. This would seem to indicate that the nature of the heteroatom has some influence on the magnitude of T_g.

Figure 4 shows the variation of ln T_g as a function of the inverse of the degree of polymerization P, following the Fox–Flory [14] treatment described for poly(styrene). Again a linear relationship is obtained for PSeM and curves for PBzM and PTiM. From these plots it is possible to determine b_T, a parameter related to the apparent activation energy for viscous flow E_T, according to the classical relation

$$T_g = T_{g(\infty)} \exp(-b_T/5M_0P) \tag{3}$$

where M_0 is the molecular weight of the monomer unit and P the degree of polymerization. It is also possible to obtain $T_{g(\infty)}$ from this equation. Table 3 summarizes the b_T and $T_{g(\infty)}$ values obtained from these plots. It can be seen that these $T_{g(\infty)}$ values are similar to those obtained using eqns. (1) and (2). The values of b_T are higher than those previously reported for other aromatic poly(methacrylates) [7] but the value for PSeM is similar to that

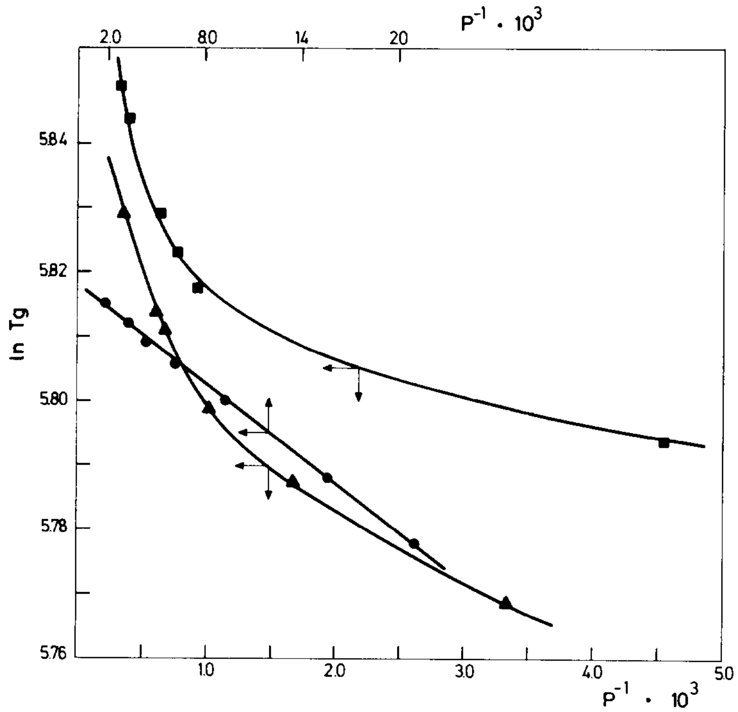


Fig. 4. Variation of ln T_g with the inverse of the degree of polymerization P^{-1} for PBzM (▲), PTiM (■) and PSeM (●).

reported for poly(methyl methacrylate) (2.1 kcal mol^{-1}) [7]. On the basis of these results we can assume that the temperature coefficient of the viscosity depends on the side chain structure of the polymer, as has been found for other groups of vinyl polymers [7]. This behaviour has been explained in terms of the rate of internal relaxation (mobility), which depends on the internal configurational structure (and on the associated free volume). Therefore the influence of the side chain structure should be reflected in b_T, as it is in this family of polymers.

TABLE 3

Values of $T_{g(\infty)}$ and b_T for PBzM, PTiM and PSeM, obtained from eqn. (3)

Polymer	$T_{g(\infty)}$ [a] (K)	b_T (kcal mol^{-1})	$T_{g(\infty)}$ [b] (K)
PBzM	345	40.6	–
PTiM	353	50.3	357
PSeM	333	2.2	349

[a] Obtained from the straight line.

[b] Obtained from the curve.

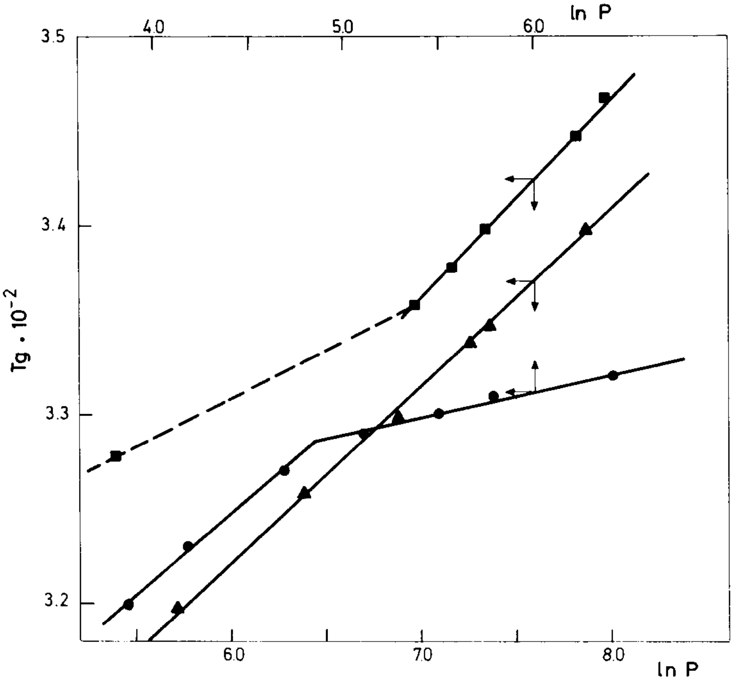


Fig. 5. Variation of T_g with ln P for PBzM (▲), PTiM (■) and PSeM (●).

On the other hand, a linear relationship is found between T_g and the logarithm of the degree of polymerization [7,8,19], according to the relation

$$T_g = T_g(0) + K' \ln P \tag{4}$$

where K' is a parameter dealing with the polymer structure and $T_g(0)$ the characteristic temperature of the monomer unit related to the apparent T_g of the monomer. Figure 5 shows the variation of T_g with ln P. Clearly, linear relationships are obtained, but for PTiM and PSeM two regimes are observed with a critical value of molecular weight after which the variation of T_g follows a different trend. Similar results have been found in the case of poly(styrene) over a wide range of molecular weights [19] where three values for K' are obtained, and recently for some poly(methacrylates) of very low molecular weights [20]. In the case of PBzM, a linear relationship is obtained with only one value for K'. Table 4 summarizes the values of $T_g(0)$ obtained by extrapolation to $P = 1$ taking into account both regimes for PSeM and PTiM. These $T_g(0)$ values seem to be overestimated if we take into account that the monomers are liquids at room temperature. Nevertheless, a direct correlation between $T_g(0)$ and the rigidity factor σ is found, i.e. $T_g(0)$ increases as the rigidity factor increases. This result could be a consequence of the effect of the heteroatom on the conformational behaviour of these polymers, which seems to be the principal factor influencing their thermal behaviour and more important than other parameters of the lateral group

TABLE 4

Values of $T_g(0)$ and K' obtained from Fig. 5 by extrapolation to $P=1$ for PBzM, PTiM and PSeM

Polymer	$T_g(0)$ [a] (K)	$T_g(0)$ [b] (K)	K' [a]	K' [b]
PBzM	267	–	9.21	–
PTiM	287	301	7.23	5.03
PSeM	317	287	2.31	8.47

[a] From first regime.

[b] From second regime.

such as molecular volume V or aromaticity A. It would be interesting to compare the thermal behaviour of a more extended family of these chalcogenides containing polymers. Unfortunately the oxygen-containing polymers furfuryl (PFM) and tetrahydrofurfuryl (PHFM) are insoluble and it is therefore not possible to obtain fractions of different molecular weights in order to investigate the influence of molecular weight on thermal behaviour. Nevertheless, the insoluble polymers show higher T_g values, i.e. 384 and 378 K for PFM and PHFM, respectively. If we assume that these are $T_{g(\infty)}$ values we can suggest a correlation between chalcogenides containing polymers, in the sense that T_g decreases as the atomic volume of the hetero atom increases and the molar volume of the side ring decreases.

CONCLUSIONS

The results of this study indicate that the various T_g–M_n relationships show deviation from linearity for PBzM and PTiM. Linear relationships are found for PSeM, but this is probably due to the narrow range of molecular weights used. Nevertheless, the values for $T_{g(\infty)}$ obtained using the various relationships (including the exponential Fox–Flory equation [14]) are similar, which would indicate that these relations are useful for this purpose. The b_T parameter, which is related to the apparent activation energy of viscous flow E_T, can be determined using the Fox–Flory equation. A linear relationship is found for the variation of T_g and ln P. This seems to be a general relation for different families of polymers [7,8] but it would be necessary to cover a wider range of molecular weights to confirm that this is the case. The nature of the side chain structure has been found to have a marked effect on $T_{g(\infty)}$, $T_g(0)$, b_T, and K'.

ACKNOWLEDGEMENTS

We express our thanks to Direccion de Investigación (DIUC), Pontificia Universidad Católica de Chile and Fondo Nacional de Ciencias (Fondecyt) for partial financial support.

REFERENCES

1 I. Brandrup and E.H. Immergut (Eds.), Polymer Handbook, Wiley, New York, 1975, p. III-139.
2 M. Yazdani-Pedram, E. Soto, L.H. Tagle, F.R. Díaz, L. Gargallo and D. Radić, Thermochim. Acta, 105 (1986) 149.
3 L. Gargallo and M. Russo, Makromol. Chem., 176 (1975) 2735.
4 G. Pizzirani, P. Magagnini and P. Giusti, J. Polym. Sci., A-2 (1971) 1133.
5 J.M.G. Cowie and P.M. Toporowski, Eur. Polym. J., 4 (1968) 621.
6 J. San Román, E.L. Madruga and J. Guzmán, Polym. Commun., 25 (1984) 373.
7 L. Gargallo, N. Hamidi and D. Radić, Thermochim. Acta, 114 (1987) 319.
8 L. Gargallo, E. Soto, L.H. Tagle and D. Radić, Thermochim. Acta, 130 (1988) 289.
9 L. Gargallo, M.I. Muñoz and D. Radić, Polymer, 27 (1986) 1416.
10 F.R. Díaz, L.H. Tagle, L. Gargallo, D. Radić, M.I. Muñoz and J.B. González, Makromol. Chem. Rapid Commun., 7 (1986) 553.
11 L. Gargallo, M.I. Muñoz, F.R. Díaz and D. Radić, Polymer, 29 (1988) 1898.
12 L. Gargallo, M.I. Muñoz and D. Radić, Polym. Bull., 10 (1983) 264.
13 F. Fringuelli, G. Marino, A. Taticchi and G.J. Grandolini, J. Chem. Soc., Perkin Trans. II, (1974) 332.
14 T.G. Fox and P.J. Flory, J. Appl. Phys., 21 (1950) 581.
15 K. Ueberreiter and G.Z. Kaning, Naturforscher 6 (1961) 551.
16 R.F. Fedors, Polymer, 20 (1975) 297.
17 R.F. Boyer, Macromolecules, 7 (1974) 142.
18 J.E.L. Roovers and P.M. Toporoski, J. Appl. Polym. Sci., 18 (1975) 1685.
19 P. Claudy, J.M. Létoffé, Y. Camberlain and J.P. Pascault, Polym. Bull., 9 (1983) 208.
20 B. Boutevin, Y. Pietrasanta, L. Sarraf and H. Snoussi, Eur. Polym. J., 24 (1988) 539.