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EFFECT OF THE SIDE CHAIN STRUCTURE ON THE GLASS TRANSITION TEMPERATURE.
2. POLY(*o*-ALKYLPHENYL METHACRYLATE)S

L. GARGALLO, N. HAMIDI and D. RADIĆ *

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

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ABSTRACT

The glass transition temperature (T_g) of poly(phenyl)-, poly(2,6-dimethylphenyl)-, and poly(2,6-diisopropylphenyl)methacrylates, have been measured by DSC. The effect of the nature of the ring substituents on T_g are discussed. Equations for relating glass transition temperatures to average molecular weight ($\bar{M}$) are examined. Non-linear dependence between T_g and $\bar{M}^{-1}$ is found, but the relationship between T_g and log M (M = molecular weight) shows a linear dependence. The $T_{g(\infty)}$ values for the polymer studied are determined.

INTRODUCTION

It has been demonstrated that the flexibility, bulkiness and polarity of the pendant groups attached to the main chain of a polymer can play an important role in determining glass transition temperatures (T_g) because this temperature indicates the onset of long-range cooperative chain motion in the polymer sample. In the case of aromatic vinyl polymers, the introduction of flexible groups like carbonyl, ester or ether linkages between the aromatic groups and the main chain produces a noticeable effect on T_g [1–4]. On the other hand, different relationships between T_g and number average molecular weight ($\bar{M}_n$) have been developed by different authors [5–7]. Fox and Flory [5] have reported a linear equation of the form

$$T_g = T_{g(\infty)} - (K/M) \tag{1}$$

where T_g is the glass transition temperature for a liquid with a molecular weight M, $T_{g(\infty)}$ is the corresponding glass transition temperature for an infinitely large molecular weight, and K is a constant characteristic of a given polymer. Moreover there is evidence that K is not constant when data

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* Author to whom correspondence should be addressed.

for polymers covering an extended range of molecular weight are compared to eqn. (1) [6,8,9]. Fedors [6] has found a similar equation in form to eqn. (1) which can be used to represent T_g–M data over the entire range of M. This equation is expressed by

$$T_g = T_{g(\infty)} - (A/M + B) \tag{2a}$$

and can be expressed equivalently in terms of P, the degree of polymerization by

$$T_g = T_{g(\infty)} - (A'/P + B') \tag{2b}$$

where A and B are parameters, $A' = A/M_0$, $B' = B/M_0$ and M_0 is the molecular weight of the repeating unit. This equation has been tested for a wide range of polymers and the results show good agreement.

The aim of this work was to study the effect of the side-chain structure of aromatic-group containing methacrylate polymers on the glass transition temperatures. In addition, the T_g–M relationships for poly(phenyl) (PPh), poly(2,6-dimethylphenyl) (PDMP) and poly(2,6-diisopropylphenyl) (PDPP) were analysed in order to check the applicability of the different equations.

EXPERIMENTAL

Monomer and polymer preparation

Monomer and polymer preparations and characterizations were performed according to the technique described previously [10,11]. All the polymerizations were done under the same conditions in order to ensure similar tacticities.

Molecular weight determination

The number-average molecular weight ($\overline{M}_n$) was determined at 298 K in chlorobenzene by osmometry using a Hewlett Packard high-speed membrane osmometer Model 502, with a variable temperature control. The weight-average molecular weight ($\overline{M}_w$) and the polydispersity index ($\overline{M}_w/\overline{M}_n$) of the polymer samples were determined by size-exclusion chromatography (SEC), using a Perkin Elmer high performance liquid chromatograph (HPLC) equipped with a 6000-psi (0.84 Pa) pump, a Perkin Elmer differential refractometer model LC 25 and an injector of 175 μl. Three Water Associates Ultra Styragel Columns (10^3 Å and 10^5 Å) in series were used. Tetrahydrofuran was used as eluent and the flow rate was 1 ml min^{-1}. The columns were first calibrated with standard polystyrene samples of narrow molecular-weight distribution. Calibration curves of the type log $M = f(V_e)$, where V_e is the peak elution volume of the polystyrene standard, were used. The $\overline{M}_w$ and $\overline{M}_n$ values of the polymers were calculated with the aid of a computer program based on normalization of the chromatograms [4].

Differential Scanning Calorimetry (DSC)

The glass transition temperatures (T_g) of polymer samples were 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 aluminum pans. Dry nitrogen was used as a purge gas and thermograms were measured 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 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 T_g was estimated from the point of intersection of the sloping portion of the curve resulting from the baseline shift.

RESULTS AND DISCUSSION

Studies of the glass transition temperatures of poly(phenylacrylate)s [3,12], poly(phenylmethacrylate)s [3] and poly(vinylbenzoate)s [13,14] have demonstrated that the T_gs of these types of polymers are strongly influenced by the nature of the side groups. However, when comparing glass transition temperatures of different polymers it is necessary to ensure molecular weights above which T_g becomes independent of molecular weight and to have samples with similar tacticities. If the molecular weight is not high enough to reach a constant T_g, it is necessary to obtain a T_g value at infinitely large molecular weight at which T_g becomes constant ($T_{g\infty}$).

Table 1 shows the T_g values for fractions of different molecular weights (or degree of polymerization, P) for the polymers studied, i.e., poly(phenylmethacrylate) (PPh), poly(2,6-dimethylphenylmethacrylate) (PDMP), poly(2,6-diisopropylphenylmethacrylate) (PDPP). The polydispersity index of the fractions ($\overline{M}_w/\overline{M}_n$) are in the range 1.1–1.3. These results show that the T_g value increases as the bulkiness of the side groups increase in the order: diisopropylphenyl > dimethylphenyl > phenyl. This behaviour is the same for different samples of similar molecular weight.

Figure 1 shows the variation of T_g with molecular weight for the three polymers studied. This figure shows a normal behaviour in the sense that T_g increases as the molecular weight increases reaching a constant value which is designated as $T_{g(\infty)}$.

TABLE 1

Glass transition temperatures, T_g, weight average molecular weight, $\overline{M}_w$ (GPC), and degree of polymerization, P, for different fractions of PPh, PDMP and PDPP

	Fractions							
	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8
PPh ($T_{g(\infty)}$ = *403 K*)								
$10^{-5}\overline{M}_w$ [a]	18.50	11.50	8.40	4.06	3.15	2.45	1.31	0.45
$10^{-3}P$	11.40	7.10	5.20	2.50	1.93	1.52	0.81	0.28
T_g(K)	398	394	391	384	382	381	372	362
PDMP ($T_{g(\infty)}$ = *462 K*)								
$10^{-5}\overline{M}_w$ [a]	2.38	0.87	0.55	0.30	0.18			
$10^{-3}P$	1.25	4.58	2.88	1.56	0.97			
T_g(K)	449	434	425	420	388			
PDPP ($T_{g(\infty)}$ = *471 K*)								
$10^{-5}\overline{M}_w$ [a]	4.03	3.02	2.44	1.87	1.00	0.53	0.13	
$10^{-3}P$	1.64	1.23	0.93	0.76	0.41	0.22	0.05	
T_g(K)	460	457	455	453	443	437	395	

[a] Determined by GPC.

In order to obtain a T_g value at which T_g becomes constant $T_{g(\infty)}$, we plotted T_g versus $\overline{M}^{-1}$ (or P^{-1} dotted lines) according to the classical relation proposed by Fox and Flory [5] (eqn. 1), see Fig. 2. It can be seen from Fig. 2 that straight lines are not obtained from the Fox and Flory [5]

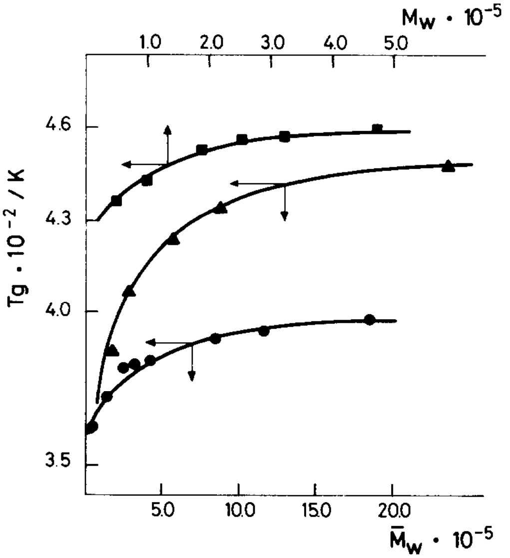

Fig. 1. Variation of T_g with the weight-average molecular weight, $\overline{M}_w$, for PPh (●), PDMP (▲) and PDPP (■).

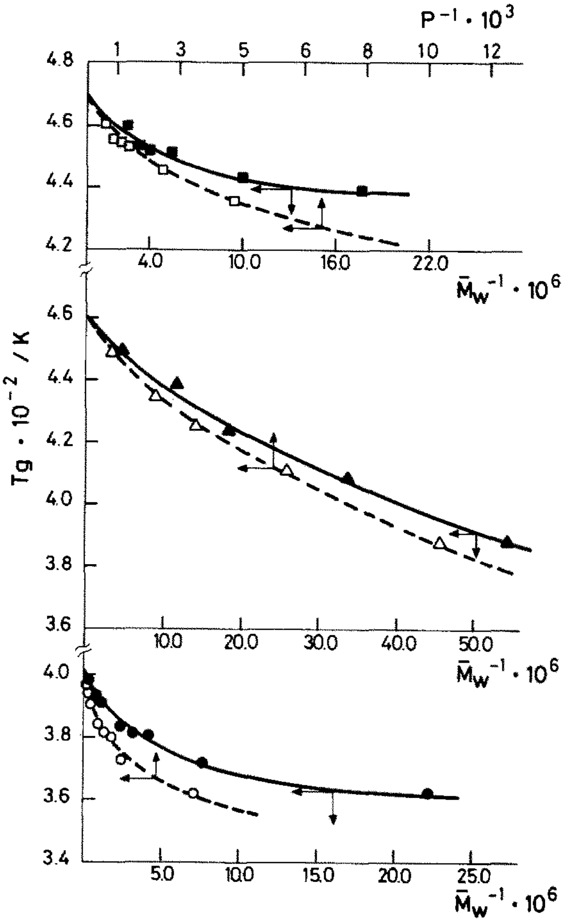

Fig. 2. Variation of T_g with the inverse of molecular weight $\bar{M}_w^{-1}$ (———) and the degree of polymerization P^{-1} (— — —), for PPh (●), PDMP (▲) and PDPP (■) according to eqns. (1) and (2).

representation. It is difficult to get $T_{g(\infty)}$ by extrapolation to infinite molecular weight. A similar behaviour has been reported by Fedors [6] for different polymers. The results of Fig. 2 show that the T_g–M (or T_g–P) data confirm eqn. (2) proposed by Fedors for all the polymers studied over the entire range of M. According to these plots the values of $T_{g(\infty)}$ obtained for PPh, PDMP and PDPP are summarized in Table 2. These values were obtained by extrapolating the curves of Fig. 2 to infinite molecular weight. The results show that the shape of the curves are in good agreement with that obtained by Fedors [6].

It is interesting to note that eqn. (1) of Fox and Flory [5] would predict that the data be linear with a negative slope; as may be seen in this case, this is decidedly not true. On the other hand if we extrapolate the experimental

TABLE 2

Values of infinite glass transition temperature $T_{g(\infty)}$, determined by using eqns. (1–3) and extrapolating the curve or straight line considering only high molecular weight, the rigidity factor σ [e], and the molar volume of the side group, V

Polymer	$T_{g(\infty)}$ (K)				σ [e]	V (cm^3)
	a	b	c	d		
PPh	403	404	403	404	2.40 [f]	0.933 [g]
PDMP	462	455	461	457	2.61 [g]	1.016 [g]
PDPP	471	468	472	466	3.88 [g]	1.040 [g]

[a] Determined by extrapolation of the curve using eqn. 1 or 2.

[b] Determined by extrapolation of the straight line using eqn. 1 or 2 for high molecular weight.

[c] Determined by extrapolation of the curve using eqn. 3.

[d] Determined by extrapolation of the straight line using eqn. 3 for high molecular weight.

[e] $\sigma = (\langle r^2 \rangle_0 / \langle r^2 \rangle_{0f})^{1/2}$.

[f] From ref. 16.

[g] From ref. 10.

values as a straight line, taking into account only high molecular weights, we obtain $T_{g(\infty)}$ for PPh, PDMP and PDPP. The values are summarized in Table 2, column 2. These values are rather similar to those obtained using eqn. (2) although these $T_{g(\infty)}$ values are slightly lower.

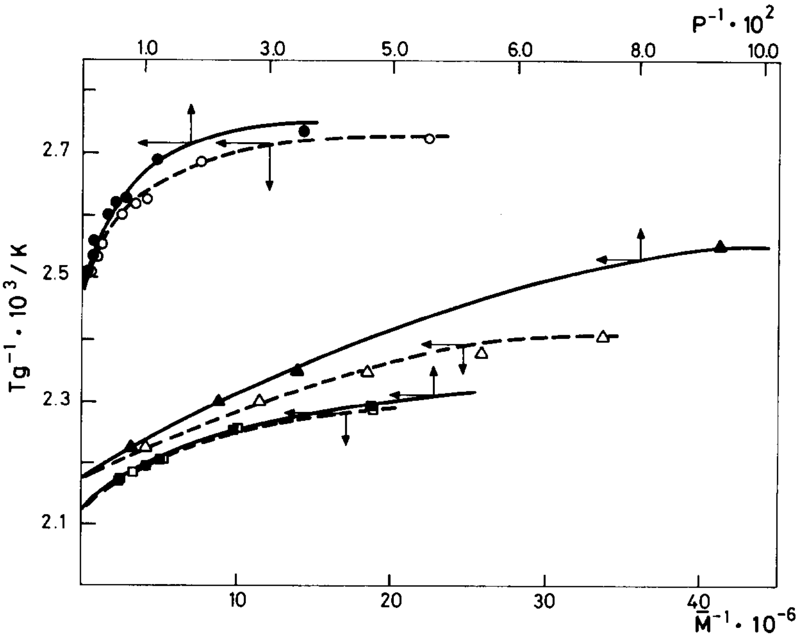

Fig. 3. Variation of T_g^{-1} with the inverse of molecular weight $\bar{M}_w^{-1}$ (———) and the degree of polymerization P^{-1} (— — —), for PPh (●), PDMP (▲) and PDPP (■) according to eqn. (3).

Figure 3 shows the variation of T_g^{-1} as a function of the inverse of the molecular weight (M) or degree of polymerization P, according to the relation proposed by Roovers and Toporowsky [15].

$$1/T_g = (1/T_{g(\infty)}) + (c/P) \tag{3}$$

According to Fig. 3 the $T_{g(\infty)}$ values for PPh, PDMP, PDPP are 403, 461 and 472 K, respectively. These values have been obtained by extrapolation to an infinite degree of polymerization, taking the curve which best fits the experimental data; these results are also summarized in Table 2, column 3. These results are quite similar to those obtained by extrapolation using eqn. (2). If we extrapolate the experimental data to infinite molecular weight and take into account only the T_g values for samples with high molecular weight, a straight line is obtained from which it is possible to get $T_{g(\infty)}$ which is summarized in column 5 of Table 2. These findings are rather different to those obtained by extrapolating the curve, but they are similar to those obtained using eqn. (1).

It is interesting to note that the $T_{g(\infty)}$ value increases as the rigidity factor σ and molar volumes V of the side chain increase, as is expected according to the literature [17], and they reach a constant value. This finding is independent of the method employed to determine $T_{g(\infty)}$.

On the other hand, a linear relationship is obtained when T_g values for the different fractions of the polymers studied are plotted versus log M (see

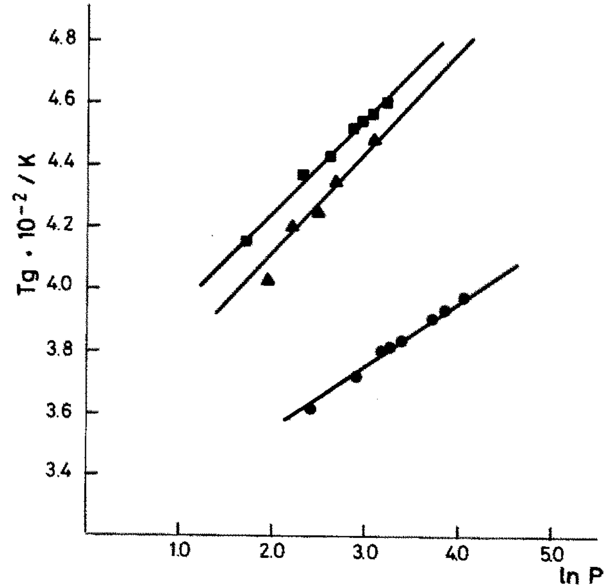

Fig. 4. Variation of T_g with log P for PPh (●), PDMP (▲) and PDPP (■) according to eqn. (4b).

Fig. 4). This behaviour agrees with an equation of the form:

$$T_g = A + k \ln M \tag{4a}$$

where A and k would be parameters depending on the structure of the polymers. Equation (4a) can alternatively be written as:

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

where $T_g(0)$ is a temperature characteristic of the monomer unit, i.e., the apparent T_g value of the monomer. These findings agree with that obtained in Fig. 1(b) where the variation of the glass transition temperature with the molecular weight shows a similar behaviour in the sense that the extrapolation of the curves to a low degree of polymerization ($P \rightarrow 1$) gives a very similar $T_g(0)$ value to that obtained according to Fig. 4. The k' values obtained from the slopes of these plots and the $T_g(0)$ values obtained by extrapolation to $P = 1$ show a reasonable linear dependence with the $T_{g(\infty)}$ value obtained by the different methods. $T_g(0)$ increases in the same trend as the $T_{g(\infty)}$ values, i.e., as the steric hindrance of the side chain increases. These results are summarized in Table 3. The $T_g(0)$ values obtained by extrapolation are higher than those of the melting points of the monomers; this could be due to the fact that the molecular weights considered in this study are high. In the case of polystyrene [18], three regimes can be seen in the dependence of T_g on the degree of polymerization. Therefore the extrapolation of $P \rightarrow 1$ in these systems could overestimate the $T_g(0)$ values. For this reason it is very difficult to think in terms of a special kind of T_g, which would be a consequence of some molecular relaxation process, taking place in the glass state of the monomers, and as a consequence of intramolecular interactions.

Taking into account the Fox and Flory [5] theory of the second-order transition temperature and related properties of polystyrene, especially the influence of the molecular weight, the relationship between T_g and M (or P) can be expressed by:

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

where b_T is a parameter which is related to E_T, the apparent activation

TABLE 3

Values of $T_g(0)$, k' and b obtained from Fig. 4 and eqn. (5)

Polymer	$T_g(0)$ (K)	k'	b_T	$T_{g(\infty)}$ [a] (K)
PPh	316	20.3	~15	391
PDMP	347	30.0	13.8	450
PDPP	364	32.3	19.7	461

[a] Calculated from eqn. (5).

energy for viscous flow; M_0 is the molecular weight of the monomer unit; and P is the degree of polymerization. According to eqn. (5) a plot of ln T_g against the inverse of the degree of polymerization (P^{-1}) should give the value of b_T and $T_{g(\infty)}$. Table 3 also summarizes the b_T and $T_{g(\infty)}$ values obtained from these plots. The $T_{g(\infty)}$ values so obtained are in good agreement with those given in Table 2. Straight line plots were obtained for PDMP and PDPP, but for PPh a curve was obtained; therefore the b_T and $T_{g(\infty)}$ values were obtained by taking into account only high molecular weight values. We also calculated the b_T value for poly(methylmethacrylate) (PMMA) taking the T_g values from the literature [19]. The b_T values so obtained show that PDMP presents a lower value than that of PPh and PDPP and the lowest value is obtained for PMMA (2.1 kcal mol^{-1}). This result means that the temperature coefficient of the viscosity depends on the side-chain structure of the polymer, at least in this family. This behaviour could be due to the fact that the rate of internal relaxation (mobility) depends primarily on the internal configurational structure (and on the associated free volume). According to the thermal behaviour of the different fractions of the polymers studied, there is a marked influence of the side-chain structure on the glass transition temperature and their dependence with the degree of polymerization, as is expected.

CONCLUSION

It is concluded from this study that the glass transition temperatures of poly(*o*-alkylphenylmethacrylate)s are greatly influenced by the rigidity, bulkiness and molar volume of the pendant group. The dependence of T_g on molecular weight does not conform to the classical equation of Fox and Flory [5] but agrees with that proposed by Fedors [6]. A reasonable linear dependence is found when T_g is plotted versus log P and the extrapolation of $P \rightarrow 1$ gives $T_g(0)$, a parameter which is characteristic of the monomer unit. This parameter also shows a linear dependence with $T_{g(\infty)}$. Although the dependence of T_g with $\overline{M}^{-1}$ is not linear, it is possible to determine a $T_{g(\infty)}$ value for the different polymers which shows a noticeable dependence on the structure. These $T_{g(\infty)}$ values are in good agreement with those obtained by using the exponential Flory and Fox equation [5]. The b_T parameter, which is related to apparent activation energy for viscous flow, E_T, is determined from the Fox and Flory equation and this parameter apparently depends on the structure of the polymer.

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