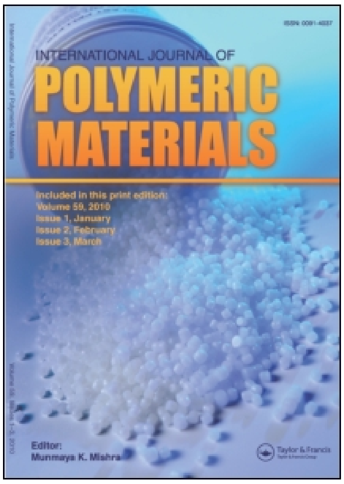

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Thermal Behaviour of Poly(methacrylates) Containing Indanyl Groups

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Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) of poly(methacrylates) containing indanyl moieties were performed. Different Tg-Mn relationships have been established in order to obtain the glass transition temperature in the limit of high molecular weight Tg_{∞}, using samples of different number average molecular weight (Mn). Non linear dependence between Tg and Mn using different relationships is found. The values of Tg_{∞} is correlated with the chain rigidity parameters for these polymers. Thermogravimetric analysis shows different degradation profiles depending on the structure of the side chain of the polymer.

Keywords: Polymethacrylates; indanyl; synthesis; thermal analysis

INTRODUCTION

The effect of the polymer side chain structure on the glass transition temperature, Tg, has been previously reported for a number of systems [1–4]. In aromatic vinyl polymers the introduction of flexible groups like carbonyl, ester or ether linkages between the aromatic groups and the main chain produce a noticeable effect on Tg [5–8]. There are significative differences in the thermal behaviour of polymers containing aliphatic, aromatic or saturated rings in the side chain, which in turn is related to the flexibility or

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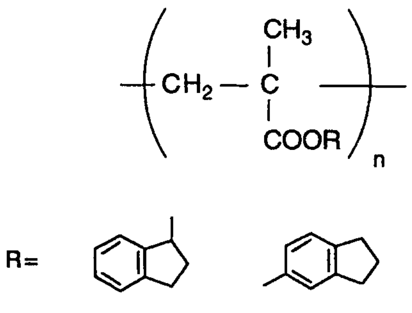
rigidity of the main chain due to the effect of the substituents. Generally bulky side chain polymers are rigid with high thermal stability, high Tg values and the bulkiness is mainly obtained by the insertion of aromatic rings as side chains. The flexibility, bulkiness, and polarity of pendant groups attached to the main chain play an important role in determining Tg since this temperature reflects the onset of the long range cooperative chain motion in the polymer sample. In order to obtain the critical value of the chain length at which Tg becomes constant (Tg_{∞}) several relationships have been developed to describe the variation of Tg with Mn. The Flory Fox [9], relationship is one of the most widely used. This equation considers a linear dependence between Tg and the inverse of Mn, but important deviation from the linearity is observed, mainly at high molecular weights [2,9–12]. Fedors [10], has proposed an equation similar to that of Fox and Flory which can represent Tg-Mn data over the entire range of molecular weights. A linear relationship between Tg^{-1} and Mn^{-1} was reported by Roovers and Toporowsky [13]. These empirical relationships are important to determine Tg_{∞} values in order to perform a thermal characterization of the polymer samples. On the other hand the thermal stability of polymers depends, on the polymer structure and the type of substituents in the main chain. The effect of the side chain structure on the thermogravimetric behaviour of poly(methacrylates), poly(itaconates) and copolymers containing different bulky side chains has been previously reported [4,14,15] and it is possible to find a correlation between the temperature of thermal decomposition and the volume and rigidity of the side chain.

The aim of this work is to report the variation of Tg with number average molecular weight Mn, in Poly(1 and 2 indanyl methacrylate) (P1IM and P5IM, see scheme 1) in order to study the effect of the cyclic spacer group on Tg and on the thermal stability of these polymers. The validity of the classical Tg-Mn relationships is also discussed.

EXPERIMENTAL

Monomer and Polymer Preparation

1-indanyl and 5-indanyl methacrylate were obtained by esterification of methacryloil chloride with the corresponding indanols according to the methods previously reported [16,17]. Polymers were obtained by radical polymerization in toluene solutions at 333 K. Polymers were fractionated and characterized by viscometry and light scattering [16, 17].



1-Indanyl (P1IM)

5-indanyl (P5IM)

Scheme

DSC Measurements

The glass transition temperatures (Tg) of the polymers were measured with a Mettler TA-3000 system equipped with a TC-A 10 Processor with DSC-20 cell. Polymer samples were dried under reduced pressure in a vacuum oven prior measurements. Samples were weighted into the DSC aluminum pans. Dry nitrogen was used as purge gas and thermograms were measured in the range 308 K to 450 K at a scan rate of 10 K/min. Regular calibration of the instrument was carried using pure metal standards.

TGA Measurements

Dynamic thermogravimetric analysis were determined using a Mettler TA-3000 calorimetric system equipped with a TC-10A processor, a TG-50 thermobalance with a Mettler MT5 microbalance. The samples were heated on Al_2O_3 pans. Measurements were carried out between 303 K and 1000 K at a 20° min^{-1} under N_2.

RESULT AND DISCUSSION

The main factor to be taken into account when comparing glass transition temperatures of different polymers, is to ensure that polymers have molecular weights above which Tg becomes independent of the degree of polymerization, and to have samples with similar tacticities. DSC measurements were performed for several fractions of P1IM and P5IM. The values of Tg for fractions of different number average molecular weights (or degree of polymerization) and low polymolecularity indices are summarized in Table I. The dependence of Tg with Mn is shown in Figure 1. A normal behaviour is observed in the sense that Tg increases as the molecular weight increases. The range of molecular weights covered by fractions of P5IM, is lower than that of P1IM. Therefore, it is difficult to reach the asymptotic value for constant glass transition temperature (Tg_∞) as shown for P1IM. Figure 2 shows the variation of Tg with Mn^{-1} according to the classical equation of Flory-Fox [9]. Deviation from linearity for high molecular weights is observed, therfore the determination of Tg_∞ may be performed by extrapolation following the shape of the curve and comparing these results with that obtained from Figure 1. In order to obtain Tg_∞ by an alternative way the Roovers Toporowsky [13] treatment of the data was performed. Figure 3 represents the variation of Tg^{-1} with Mn^{-1}. Deviation from the straight line is also observed and as in the case described above the Tg_∞ value can be obtained approximately by extrapolation of the curve. Comparison of the values obtained using the different relationships should give confidence about the real Tg_∞ values. Table II summarizes the Tg_∞ values obtained using the simple asymptotic extrapolation from the Tg-Mn plots, the Flory-Fox (F-F) [9], Roovers-Toporowsky (R-T) [13] relationships. All these relationships are useful to obtain Tg_∞ but deviations from the linearity is always found mainly at high molecular weights. Unfortunately in the case of poly(indanyl methacrylates) it was impossible to obtain fractions with higher

TABLE I Tg Values, Number Average Molecular Weights (Mn), Polydispersity Indices (I) and Degree of Polymerization for P1IM and P5IM

Fraction	*Tg/K*	$Mn \diamond 10^{-5}$	$I = M_w/M_n$	$P = M_n/M_o$
		P1IM		
F1	389	5.37	1.21	2658
F2	385	4.13	1.20	2044
F3	380	2.31	1.22	1143
F4	373	0.89	1.23	440
F5	356	0.29	1.37	143
		P5IM		
F1	358	1.36	1.25	673
F2	353	1.08	1.30	535
F3	349	1.01	1.20	500
F4	348	0.71	1.13	351
F5	348	0.54	1.27	267
F6	350	0.42	1.14	207
F7	343	0.26	1.25	129

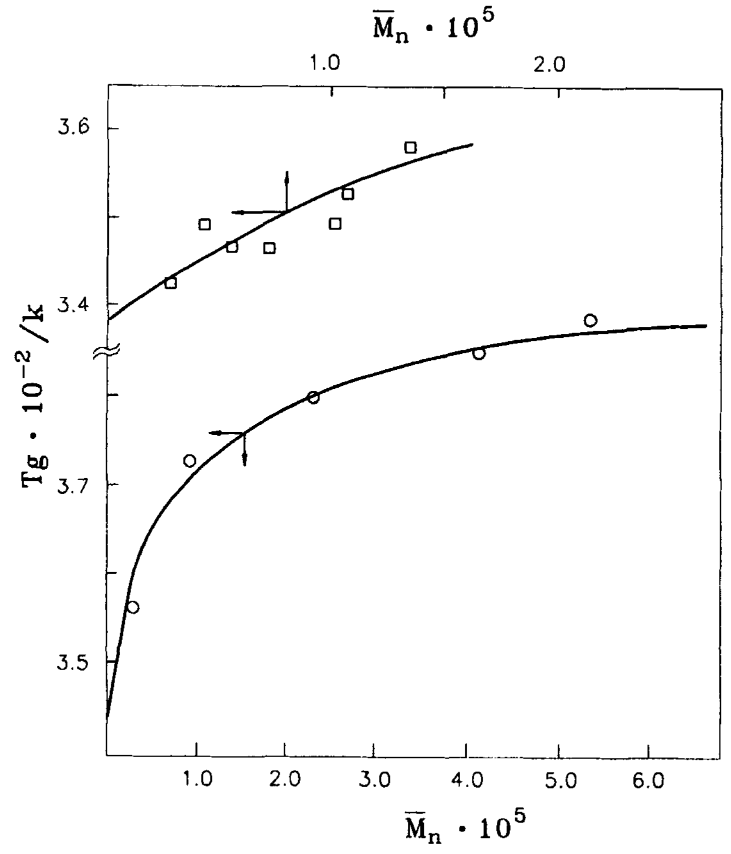


FIGURE 1 Variation of the glass transition temperature Tg with Number average molecular weight Mn for fractions of PIIM (○) and P5IM(□).

molecular weights in order to represent the variation of Tg over the entire range of values of Mn, i.e. including high and low molecular weights. Nevertheless, the Tg_∞ values obtained using the different relationships, can be considered as good Tg values and good agreement is found by using the different methods.

Good agreement is also found between the Tg_∞ values and the rigidity index σ and characteristic ratio C_∞ of PIIM and P5IM in the sense that higher Tg_∞ is found for the polymer with higher σ and C_∞ values.

Figure 4 represents the variation of Tg with the logarithm of the degree of polymerization for the different fractions of the polymer studied and a linear dependence is found. Similar results are obtained for poly(styrene) [18] and poly(alkylphenyl methacrylates) [2]. This behaviour seems to be

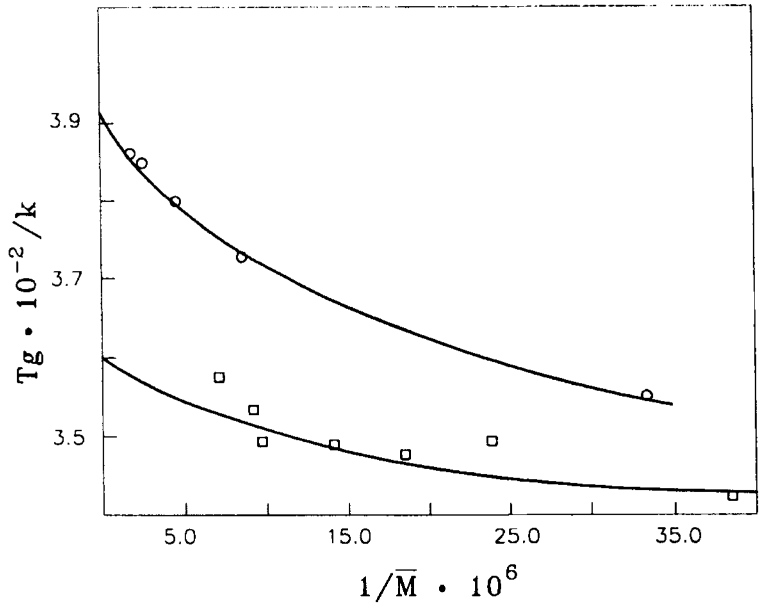


FIGURE 2 Variation of the glass transition temperature Tg with the inverse of the Number average molecular weight Mn^{-1} according to the Flory-Fox relationship, for fractions of P1IM (○) and P5IM(□).

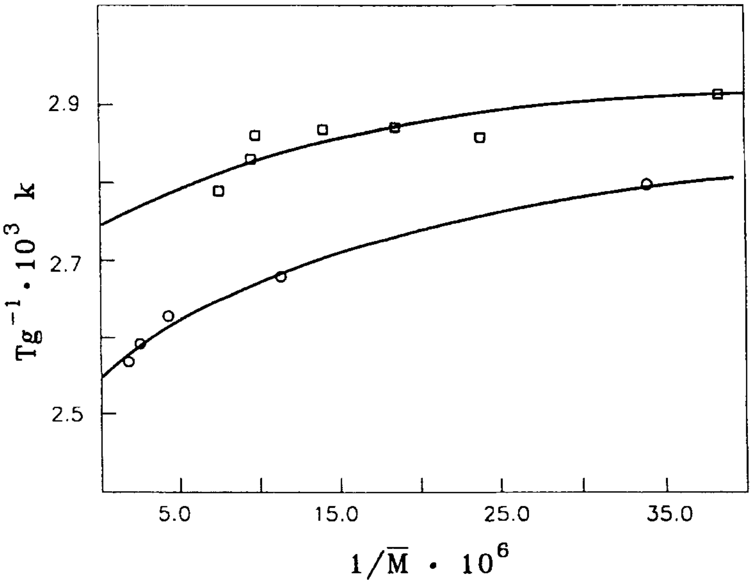


FIGURE 3 Variation of the inverse of the glass transition temperature Tg^{-1} with the inverse of the Number average molecular weight Mn^{-1} according to the Roovers Toporowsky relationship, for fractions of P1IM (○) and P5IM(□).

general according to previous results [2,4,18] which agrees with an equation of the form

$$Tg = T_{g(0)} + k\mathrm{Ln}P \tag{1}$$

where $T_{g(0)}$is a temperature characteristic of the monomer unit [2,4] and k is a constant which depends on the polymer structure and is related to the rigidity of the polymer chain [2,4]. The study of this behaviour should be of interest considering a wider family of polymers. The $T_{g(0)}$ and k values obtained are summarized in Table II. The different values of k for P1IM and P5IM shown in this table are indicative of the different polymeric structure. The rigidity factor σ, the characteristic ratio C_∞ of the polymers and the molar volume V of the side chains are also collected in Table II.

Figure 5 shows the thermogravimetric curves corresponding to fractions of similar molecular weight of P1IM and P5IM. These curves represent the dependence of the loss of weight on temperature between 300 K and 800 K. Both systems show different profiles. P5IM follows a single one-stage decomposition process. However, in the case of P1IM the degradation process is more complex. In fact, in this system the profile of the thermogram suggests a two-stage weight loss on heating. It is interesting to remark that P1IM is more rigid than P5IM, moreover, the degradation process in P1IM begin earlier than in P5IM but the second step begins at slightly higher temperature. This behaviour should be attributed to differences in the side chain structure. P1Im and P5IM are isomers but in the former the aromatic ring is linked to the main chain by a cylic spacer group, while in P5IM the

TABLE II Tg_∞ values obtained using different Relationship, Tg-Mn, Flory-Fox (F-F), Roovers-Toporowsky (R-T) and Garallo-Radic' for Tg_o. Rigidity index (σ), Characteristic ratio (C_∞), Molar volume (V) and structural k parameter for P1IM and P5IM

	P1IM	*P5IM*
Tg-$\bar{M}_n$	345	338
F-F	390	360
R-T	393	365
G-R*	350	342
σ	2.66	2.58
C_∞	14.2	13.4
V (cm^3)	114.4	113.6
k	9.14	6.61

*To obtain Tg_o.

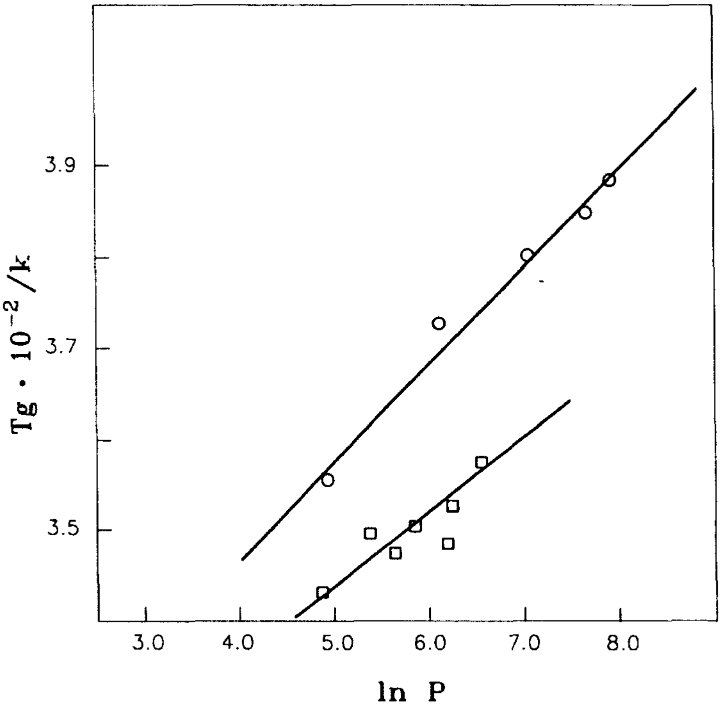


FIGURE 4 Variation of the glass transition temperature Tg with the degree of polymerization, for fractions of P1IM (○) P5IM(□).

aromatic ring is directly linked to the ester group. Therefore, the structures of the side chains have different molecular organization what should be reflected in the thermogravimetric behaviour. Table III collects the values for the initial decomposition temperature (TD^i) and the temperature at which 50% weight residual was observed ($TD^{50\%}$).

In order to determine the kinetic parameters for thermal decomposition, a multiple regression program was used. By this way the activation energy (E_a) and the frequency factor (Z) from a linear least-square fit of the data in a semilogarithmic plot were obtained. This model considers that the degradation is irreversible and that the reaction rate $d\alpha/dt$, can be expressed as function of the degree of conversion α [19,20]. The equation for this purpose can be expressed by [19,20]:

$$\beta = \mathrm{Ln}\left[\left(\frac{d\alpha/dt}{(1-\alpha)^n}\right)\right] = \mathrm{Ln}Z - \frac{E_a}{RT} \tag{2}$$

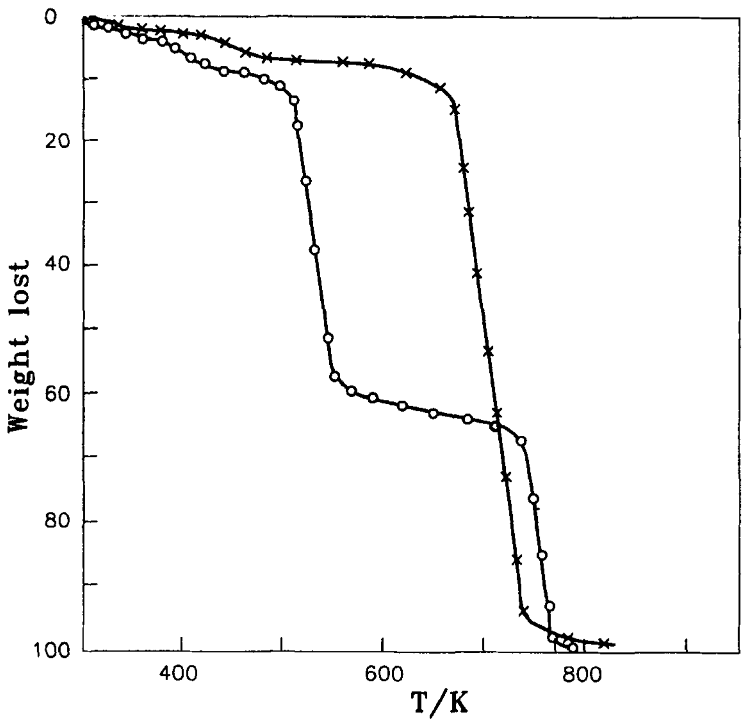


FIGURE 5 Thermogravimetric curves for P1IM (○) and P5IM (X).

E_a and Z are obtained from plots of β vs T^{-1} as shown in Figure 6 for P1IM considering two-stage weight loss and for P5IM. Table III also summarizes E_a and Z values for both polymers. Following this procedure we find a first order kinetic model for the first stage weight loss of P1IM and zero order for the second stage in P1IM and P5IM. The zero order kinetic model is frequently found for the degradation process in aromatic polymers. The activation energies obtained for P1IM are 47 and 6 Kcal/mole for the first and second stage and 22 Kcal/mole for P5IM which can be considered

TABLE III Initial decomposition temperature TD^i, temperature where the 50% of residual weight is observed $TD^{50\%}$, activation energy, the reaction order n for the degradation of P1IM and P5IM

Polymer	*TD^i K*	*$TD^{50\%}$ K*	*E_a Kcal/mol*	*n*
P1IM	490	545	47	1
	700		6	0
P5IM	630	700	22	0

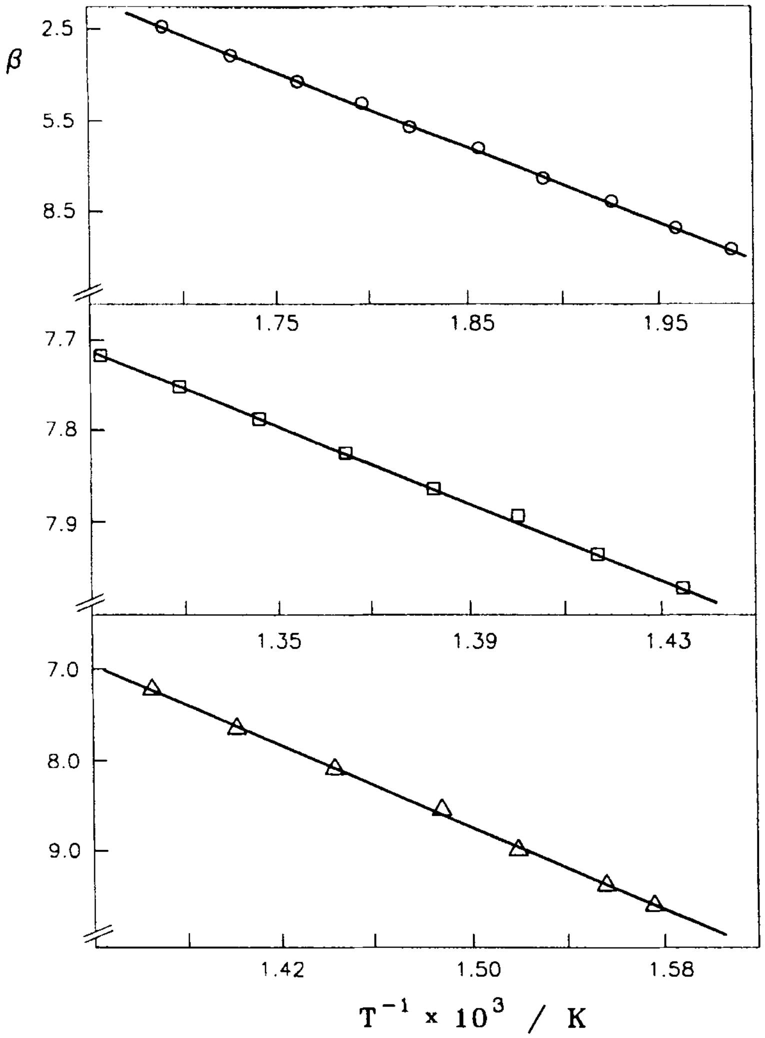


FIGURE 6 Plots of β as function of 1/T for P1IM, first stage (○), second stage (□) and p5IM (△).

as normal values in the sense that these E_a values are similar to that reported for related polymers [19,20]. The values of the frequency factor are low but in good agreement with those generally reported for a zero order kinetics [4,21].

In general is possible to conclude that a good correlation between the polymer structure and the thermogravimetric behaviour together with appropriate values of the Tg_x was found for this family of polymers.

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