Influence of molecular weight on the glass transition temperature and the melt rheological behaviour of methyl methacrylate telomers

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The synthesis of MMA telomers with different chain terminations can lead to a wide range of molecular weights. This study deals with the thermal and melt viscoelastic behaviours of such telomers. We investigated the viscosity–molecular weight relationship and took into account the chemical nature of the end group on the critical molecular weight (molecular weight beyond which entanglements occur). Two chain terminations with different chemical structures were investigated and the rheological parameters obtained with methyl methacrylate telomers were compared to those obtained with standard poly(methyl methacrylate) with the same molecular weight.

(Keywords: methyl methacrylate; telomers; glass temperature; melt viscoelasticity; entanglement; critical molecular weight)

INTRODUCTION

Telomers are usually low molecular weight compounds composed of a monomer sequence and have a well-defined chain termination. In the intermediate range of molecular weights going from the monomer to the polymer the properties of the telomers change drastically. This range of intermediate molecular weights is useful for studying structure–property relationships. For example, the viscoelastic behaviour will be greatly governed by the entanglements if the molecular weight of the telomer is larger than the critical molecular weight, M_c.

In a previous paper[1] the synthesis and molecular characterization of methyl methacrylate (MMA) telomers with different chain terminations were described. With the wide range of molecular weights synthesized it was interesting to study the variation of the thermal and viscoelastic behaviours with molecular weight.

In this study using differential scanning calorimetry (d.s.c.) measurements, we considered the effect of molecular weight on the glass transition temperature, T_g, and tried to determine the molecular weight for which the variations in the T_g *versus* molecular weight are the same for a MMA telomer as for poly(methyl methacrylate) (PMMA). Moreover we investigated the melt viscosity–molecular weight relationship to determine the M_c beyond which entanglements occur.

Two chain terminations with different chemical structures were studied and we compared the T_g and M_c values obtained for the telomers to those obtained with standard PMMA.

EXPERIMENTAL

The description of the samples and their molecular characteristics are given in *Table 1* for benzenethiol MMA telomers (C_6H_5SH) and in *Table 2* for perfluoromercaptan MMA telomers ($C_8F_{17}C_2H_4SH$).

The molecular weights were determined by gel permeation chromatography (g.p.c.) with tetrahydrofuran as solvent at room temperature. The apparatus (Waters 5900) used four microstyragel columns (1000, 500 and 2 × 100 Å) and was equipped for refractometric detection.

Table 1 Benzenethiol MMA telomers—sample designation and molecular characterization

Ref.	F01	F02	F03	F04	F05	F8	F7	F6	F5	F4
$\bar{M}_w$	210	310	410	510	610	1900	4600	6700	7300	13800
$\bar{M}_n$	210	310	410	510	610	1300	3400	5500	6000	11100
Ref.	F3	F2	F1	F9	F10	F11	F12	F13	PMMA	PMMA
$\bar{M}_w$	19100	25600	41000	11000	9600	7900	3000	1200	27000	12000
$\bar{M}_n$	14500	–	25900	–	–	–	–	–	–	–

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Table 2 Perfluoromercaptan MMA telomers—sample designation and molecular characterization

Ref.	T1	T2	T3	T4	T5	T6	T7	PMMA
$\bar{M}_w$	580	680	1100	1875	2300	5400	6700	90200
$\bar{M}_n$	580	680	895	1500	1900	4500	5300	82000

Differential scanning calorimetry measurements were carried out on a Perkin-Elmer DSC-4. The heating rate was 20°C min^{-1} and liquid nitrogen was used for cooling. The range of temperatures explored was −100 to 100°C.

Melt viscoelastic measurements were carried out using a Rheometrics mechanical spectrometer (RMS800) using the oscillatory plane–plane configuration. In such conditions it is possible to measure the variations in frequency of the loss viscosity $\eta'(\omega)$ and storage viscosity $\eta''(\omega)$ of the complex viscosity $\eta^*(\omega)$ ($\eta^* = \eta' - j\eta''$ $j = \sqrt{-1}$). In all cases the linearity of the sample response with respect to strain amplitude was verified. Nitrogen gas was used for heating to prevent thermal oxidation during the measurements. The temperatures of measurement were 150, 170, 190 and 210°C and a frequency range of $\sim 10^{-2}$–10^{2} rad s^{-1} was explored. Because of the wide range of viscosities from low- to high-molecular weight samples to be measured, a reference temperature of 170°C was chosen.

RESULTS AND DISCUSSION

Glass transition temperature and molecular weight

Benzenethiol MMA telomers. The variations in T_g values with molecular weight for benzenethiol MMA telomers are reported in *Figure 1*. In the range $210 \leqslant \bar{M}_n \leqslant 4200$ g mol^{-1} the T_g values are very dependent on molecular weight. An intermediate zone ($4200 \leqslant \bar{M}_n \leqslant 20000$ g mol^{-1}) is observed where T_g variations with molecular weight are weaker and an asymptotic value seems to be reached only at higher molecular weights ($\bar{M}_n \geqslant 20000$ g mol^{-1}). This asymptotic value corresponds to the PMMA T_g value.

Perfluoromercaptan MMA telomers. The same plot is drawn in *Figure 2* for perfluoromercaptan MMA telomers. The same behaviour as for benzenethiol MMA telomers is observed in the low molecular weight range ($580 \leqslant \bar{M}_n \leqslant 4500$ g mol^{-1}). In this case we could not observe the asymptotic tendency until the PMMA T_g value was reached because the molecular weights of the samples studied are not sufficiently high.

The most extensively studied polymer from the monomer through to the high molecular weight polymer[2] is polystyrene[3]. Chandry *et al.*[2] obtained three linear zones in the T_g variations *versus* molecular weight. The same variations were observed with poly(α-methylstyrene) and poly(dimethylsiloxane)[4]. In the case of PMMA with the same tacticity Turner[5] has shown that the T_g variations are represented by two straight lines in the low molecular weight samples. The intersection of these straight lines occurs for $M_c = \sim 8000$ g mol^{-1}.

We observed the same variations with MMA telomers but with a lower M_c. This result agrees well with the results of Boutevin *et al.*[6]. Using benzenethiol MMA telomers they have shown that the effect of the chain end mobility was strong up to a molecular weight of ~ 4000 g mol^{-1}. The same value was found by Boutevin *et al.*[7] with poly(glycidyl methacrylate).

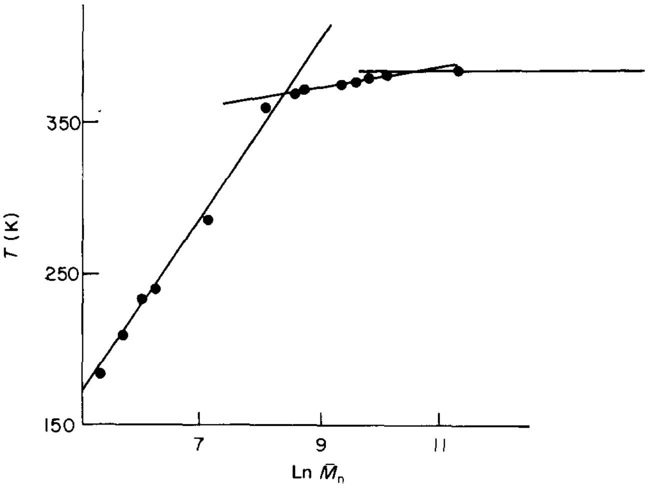

Figure 1 Variation of the glass transition temperature *versus* number average molecular weight ($\bar{M}_n$) for benzenethiol MMA telomers

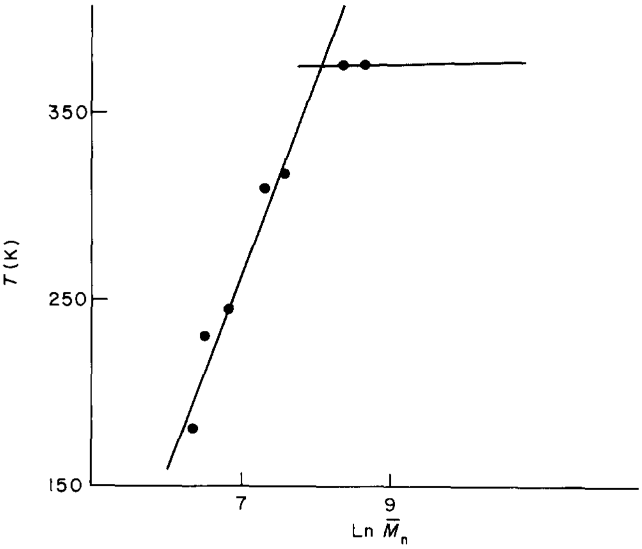

Figure 2 Variation of the glass transition temperature *versus* number average molecular weight ($\bar{M}_n$) for perfluoromercaptan MMA telomers

Melt viscoelastic behaviour

(*1*) *Benzenethiol MMA telomers. Frequency variations. Figure 3* shows the variations of the real component ($\eta'(\omega)$) and of the imaginary component ($\eta''(\omega)$) of the complex viscosity (η^*) obtained with sample F2 ($\bar{M}_w = 25600$). The temperature of the measurement is 170°C. In the low-frequency range the viscous component $\eta'(\omega)$ does not tend towards a plateau value as is usual for melt linear polymers, and the elastic component $\eta''(\omega)$ shows a double distribution. A first relaxation appears in the low-frequency range ($\omega < 10^{-1}$ rad s^{-1}) while a second relaxation occurs in the high frequency range ($\omega > 10$ rad s^{-1}). The same phenomenon is observed with all other samples. This same behaviour may exist for example with block copolymers or reinforced polymers.

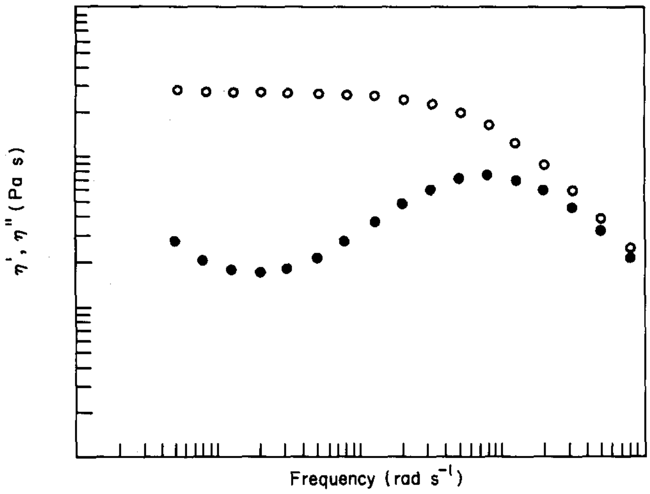

Figure 3 Variation of the real component (η', ○) and the imaginary component (η'', ●) of the complex viscosity *versus* frequency. Sample F2 ($\bar{M}_w = 25600$), $T = 170°C$

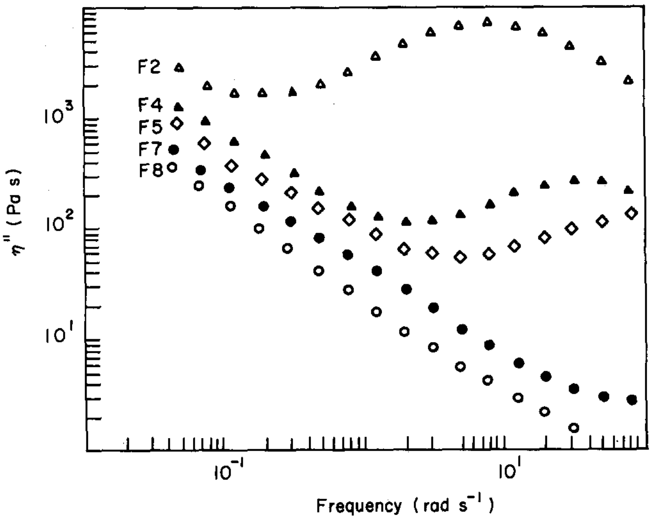

Figure 4 Variation of the imaginary component (η'') of the complex viscosity *versus* frequency for different molecular weights ($T = 170°C$)

Temperature dependence. At higher temperatures ($T > 170°C$) the same behaviour is observed but the low-frequency relaxation is shifted towards higher frequencies. At lower temperatures ($T < 170°C$) the high-frequency relaxation shifts towards lower frequencies. Consequently these two relaxations are temperature dependent and it is possible to adjust the temperature to have either low-frequency or high-frequency relaxation in the experimental frequency range studied.

Molecular weight influence. When the molecular weight is low the low-frequency relaxation is more pronounced while only the beginning of the high-frequency relaxation is visible (*Figure 4*). Moreover when the molecular weight decreases the high-frequency relaxation is shifted towards higher frequencies at the same temperature indicating that it depends on the length of the PMMA fraction (*Figure 4*). The shift towards high frequencies is equivalent to a shift towards low relaxation times ($\omega_c \tau_0 = 1$). It is well-known that the average relaxation time (τ_0) is correlated to $\bar{M}_w$ by the relation[8–10]:

$$\tau_0 = K\bar{M}_w^a \qquad (1)$$

where $a \geqslant 3$–4.

The low-frequency relaxation can be correlated with the longest relaxation times in the distribution of relaxation times. Usually the longest distribution times are dependent on the highest molecular weights in the molecular weight distribution. Because the intensity of the low-frequency relaxation is greater when the molecular weight is low it seems to depend on the ability to associate and consequently on the mobility of the end groups of the chain.

For this reason we assumed: the low-frequency relaxation depends on the ability to associate and on the degree of association of the end groups; the high-frequency relaxation is correlated with the relaxation of the PMMA fraction.

With standard PMMA a low-frequency relaxation can also be observed; its intensity is weaker than with functionalized MMA telomers. This could be due to a chain termination process during polymerization or to a very small amount of high molecular weights in the distribution[8].

(*2*) *Perfluoromercaptan MMA telomers.* A slightly different behaviour is observed with perfluoromercaptan MMA telomers. *Figure 5* shows the variations at 170°C of the viscous component $\eta'(\omega)$ and of the elastic component $\eta''(\omega)$ of the complex viscosity η^* for a sample of $\bar{M}_w = 5400\ \mathrm{g\,mol^{-1}}$. The phenomenon of double relaxation is much less pronounced. It is necessary to carry out the rheological measurements at lower temperature (150°C) to reveal the two transitions.

Critical molecular weight for entanglement. To check the previous assumption we measured the values of the Newtonian viscosity in all cases on the plateau zone of the viscous component (η') corresponding to the beginning of the high-frequency relaxation.

The variation of the Newtonian viscosity *versus* $\bar{M}_w$ is drawn in *Figure 6* for the functionalized MMA telomers and PMMA standards. The experimental points are located on a straight line [$\log \eta_0 = f(\log \bar{M}_w)$] with a slope $= 3.6$:

$$\eta_0 = 10^{-25}\bar{M}_w^{3.6} \qquad (2)$$

where $\bar{M} \geqslant 4200\ \mathrm{g\,mol^{-1}}$ and $T = 170°C$.

Two PMMA standards have been used for comparison. The first has $\bar{M}_w = 27000$ and the second has $\bar{M}_w = 12000$.

The first standard gives a Newtonian viscosity value

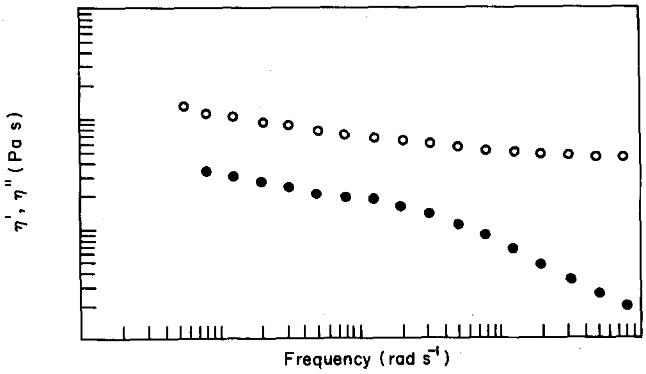

Figure 5 Variation of the real component (η', ○) and the imaginary component (η'', ●) of the complex viscosity *versus* frequency. Sample T6 ($\bar{M}_w = 5400$), $T = 170°C$

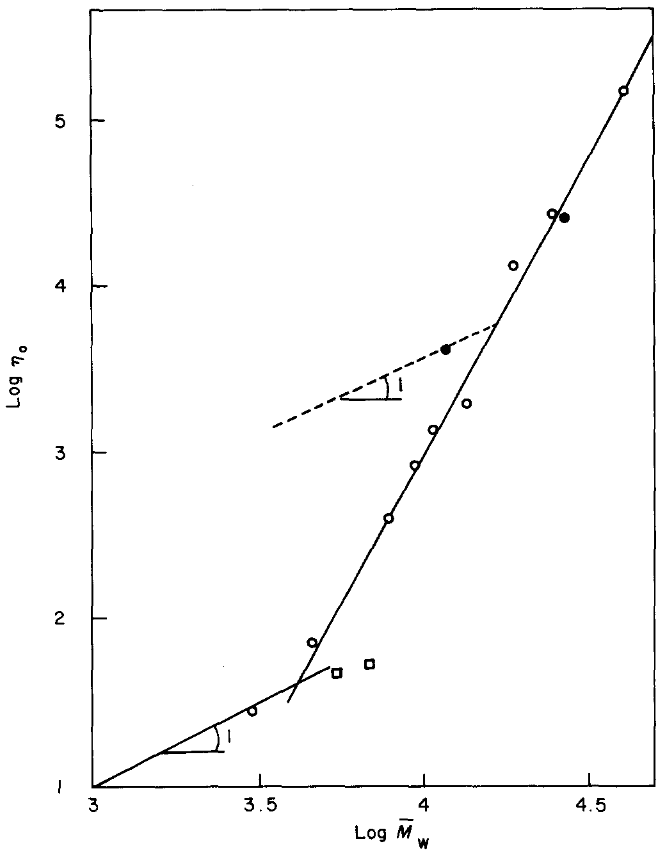

Figure 6 Variation of the Newtonian viscosity (η_0) *versus* molecular weight at 170°C; ○, benzenethiol MMA telomers; □, perfluoromercaptan MMA telomers; ●, standard PMMA

which is located on the straight line (slope = 3.6) and is in agreement with the viscosity–molecular weight relationship found for MMA telomers (equation (2)).

The second standard gives a Newtonian viscosity value which diverges from the straight line (slope = 3.6). From this value, we extrapolated a straight line with a slope = 1 (broken line). The intersection of the two straight lines with slopes = 1 and 3.6, respectively, corresponds to $\bar{M}_w = \sim 20000$. This value is in very good agreement with the theoretical value of M_c given in the literature for PMMA[8,11]. The main purpose of this representation is to show that the presence of a chemical group greatly affects M_c. With our samples the straight line with a slope = 1 seems to be reached at $M_c = \sim 4200$ illustrating the effect of chain termination on the relaxation of the MMA fraction.

It is important to note that at molecular weights higher than M_c for PMMA, the standard PMMA and the MMA telomers show the same behaviour. At lower molecular weights the ability of association of the end groups is greater as the molecular weight decreases because the PMMA chains are unentangled.

The same treatment applied to perfluoromercaptan MMA telomers shows that even at molecular weights greater than 4200 g mol^{-1} (experimental M_c for benzenethiol MMA telomers) the Newtonian viscosity values remain on a straight line with a slope = 1 (*Figure 6*). This indicates that the effect of the perfluoromercaptan termination is weaker than the effect of a benzenethiol termination.

CONCLUSIONS

Melt viscoelasticity is of great interest in the field of functionalized MMA telomers. The main conclusion is that benzenethiol MMA telomers have a M_c much lower than for PMMA homopolymers. This low M_c could be due to the association of the end groups giving rise to macromolecules with a 'star' configuration.

It is necessary to reach the M_c of PMMA to obtain the same behaviour for MMA telomers and standard PMMA. The same conclusion is valid from T_g results.

In the case of perfluoromercaptan MMA telomers the same behaviour is encountered but with a negative contribution by the end group perhaps due to the lubricating effect of the fluorinated group. Consequently, another conclusion from this work is that the chemical nature of the chain termination affects the entanglement behaviour of MMA telomers.

It is important to notice the analogy of the M_c values determined either from thermal or rheological properties. This analogy leads to the suggestion that the entanglement nature in the case of MMA telomers is perhaps different from the entanglement concept in the rheological sense and would be a reflection of interactions between the end groups.

The theoretical questions raised from this study involve interactional effects between end groups, the nature of the end groups and the entanglement behaviour of the main chain.

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