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Effect of Molecular Weight on Enthalpy Relaxation in Syndiotactic Poly(Methyl-Methacrylate)

Stefania Della Sciucca, Maurizio Penco, Luciana Sartore*

Summary: The structural relaxation behaviour of narrow fractions ($M_w/M_n < 1.1$) of syndiotactic poly(methyl methacrylate) with molecular masses ranging from 2,000 to 200,000 Daltons have been studied by DSC with two classical procedures, namely: the rate of cooling and the isothermal approaches. The apparent activation energy (Δh^*) of enthalpy relaxation was evaluated from the dependence of the glass transition temperature on the cooling rate while a comparison of the *apparent relaxation rates* was appraised from the enthalpy loss by annealing the different samples at the same level of undercooling ($T_a = T_g - 10\ °C$). As expected, the increase of molecular weights gives rise to both a continuous increase of Δh^* and a decrease of *the apparent isothermal relaxation rate.* More interestingly, both Δh^* and *the apparent isothermal relaxation rate* showed abrupt changes around the syndiotactic PMMA entanglement mass (M_e).

Keywords: apparent activation energy; enthalpy relaxation; molecular weight; relaxation rate; syndiotactic poly(methyl methacrylate)

INTRODUCTION

The structural relaxation of polymers depends on the kinetic character of the glass-transition phenomenon: amorphous polymers below their T_g are not at equilibrium and their structures continuously relax in attempt to reach the equilibrium state. Several phenomenological and molecular approaches have been proposed to describe the structural relaxation but a universal model is still lacking. The enthalpy relaxation of glasses is usually described with models developed on the basis of Tool-Narayanaswamy-Moynihan (TNM) theory[1,2]: it is assumed that the instantaneous relaxation time(s) (τ) for enthalpy relaxation depends on both the temperature (T) and the structure of the glass, identified by its fictive temperature (T_f). This approach is able to describe the enthalpy relaxation in low-molecular-weight glass-forming system fairly well,[3,4] but discrepancies have been observed in several polymeric systems.[5,6] One of these discrepancies concerns the overestimation of enthalpy lost on aging the samples for long periods of time. Hodge,[7] Gomez Ribellez[8] and Cowie[9] ascribed this features in polymers to the effect of topological constraints, such as chain entanglements, which are completely ignored in the TNM-based models.

In this work, the enthalpy relaxation of narrow fraction of syndiotactic poly(methyl methacrylate)s (PMMA) is investigated performing DSC experiments with the intention of characterize the relaxation dynamic as a function of the molecular mass and to highlight the effect of PMMA entanglement mass (M_e).

Experimental Part

The PMMA samples were purchased from Fluka (Milan, Italy) and used as received without any further purification. All of them were almost monodisperse (M_w/

Dipartimento di Chimica e Fisica per l'Ingegneria e per i Materiali. Università degli Studi di Brescia,Via Salotti 9, 25133 Brescia, Italy
E-mail: maurizio.penco@ing.unibs.it

$M_n < 1.1$). The molecular weights, the polydispersity index (PI) and the glass transition temperatures, determined according to the enthalpic definition,[10] are reported in Table 1. The molecular weight distribution (MWD) was characterized by a size exclusion chromatography (SEC) system equipped with IR and UV on-line detectors, with tetrahydrofuran (THF) as eluent (1 ml/min). The values of M_w and M_n were calculated relative to poly(styrene) standards (Polymer Laboratories, Shropshire U.K.). ^{1}H-NMR spectra were run in deuterated chloroform with a 60 MHz Variant spectrometer, using TMS as internal reference.

Differential scanning calorimetry measurements were carried out with a TA Instruments DSC series Q100. All the thermal treatments were performed on each polymer without removing the sample (about 10 mg) from the DSC.

All the experiments started at $T_g + 50\,°C$ with the sample in equilibrium. Constant cooling rate experiments were carried out in the temperature range $T_g \pm 50\,°C$ using cooling rates of 20, 10, 5, 2.5, 1.25 °C/min, each time reheating from $T_g - 50\,°C$ to $T_g + 50\,°C$ at 10 °C/min.

The annealing experiments involve three-step thermal cycles: i) cooling at constant rate ($q_c = -10\,°C/min$) from $T_g + 50\,°C$ until annealing temperature ($T_a = T_g - 10\,°C$) is reached; ii) annealing at T_a for a time t_a ranging from 60–480 min and then iii) quenching at $T_g - 50\,°C$ and reheating at a constant rate ($q_h = 10\,°C/min$) until equilibrium is again established, recording the signal. After each experiment, a reference trace of the unannealed sample was recorded to obtain the enthalpy loss due to the previous annealing.

Table 1.
Physical parameters of the investigated PMMA samples.

Sample[a)]	M_n (Dalton)	M_w (Dalton)	PI	T_g (K)
PMMA1	2,200	2,410	1.10	338.7
PMMA2	3,440	3,860	1.10	361.8
PMMA3	65,420	69,020	1.06	394.4
PMMA4	123,360	130,080	1.05	395.4
PMMA5	203,030	211,970	1.04	395.2

a) Commercial products.

Results and Discussion

In this study five different PMMA were used: the molecular weights, the polydispersity index and the glass transition temperature are reported in Table 1.

As reported in literature,[11] the entanglement mass of PMMA ranges in the interval 5,800–10,100 Dalton, depending on the stereochemical composition.

The ^{1}H-NMR analyses carried out on the samples indicate that all are predominantly syndiotactic and, in this case, the entanglement mass M_e is 5,800 Dalton.[11]

The intention here is to evaluate the apparent activation energy Δh^* of the glass transition, using the relationship existing between the temperature dependence of the relaxation time and the dependence of T_g on the cooling rate in the formation of the glass, according to equation (1):

$$\frac{\Delta h^*}{R} = \left.\frac{d\ln\tau}{d1/T}\right|_{Tg} = -\frac{d\ln|q_c|}{d1/T_f} \qquad (1)$$

where T_f is the fictive temperature determined as the crossing point of the enthalpy lines corresponding to the equilibrium liquid and to the glass (the enthalpic glass transition temperature). In this respect, a set of experiments in which the sample is cooled at different constant rates before immediately scanning in DSC is required.

In Figure 1.a and Figure 1.b such procedure is illustrated with reference to PMMA1 and PMMA5; $\Delta h^*/R$ is evaluated from the slope of the plot of $\ln[|q_c|]$ vs $[1/T_f]$, as shown in Figure 2, and the $\Delta h^*/R$ values for all the samples tested are summarized in Table 2.

The lines in Figure 2 shift towards higher temperatures as the molecular mass increases (the T_g increases with molecular mass) and the value of $\Delta h^*/R$ continuously increases with the molecular mass of the sample as shown in Figure 3. Since the relaxation is a highly co-operative process, a higher level of co-operativity and consequently higher apparent activation energy is required on going from PMMA1 to PMMA5. It is interesting to note that

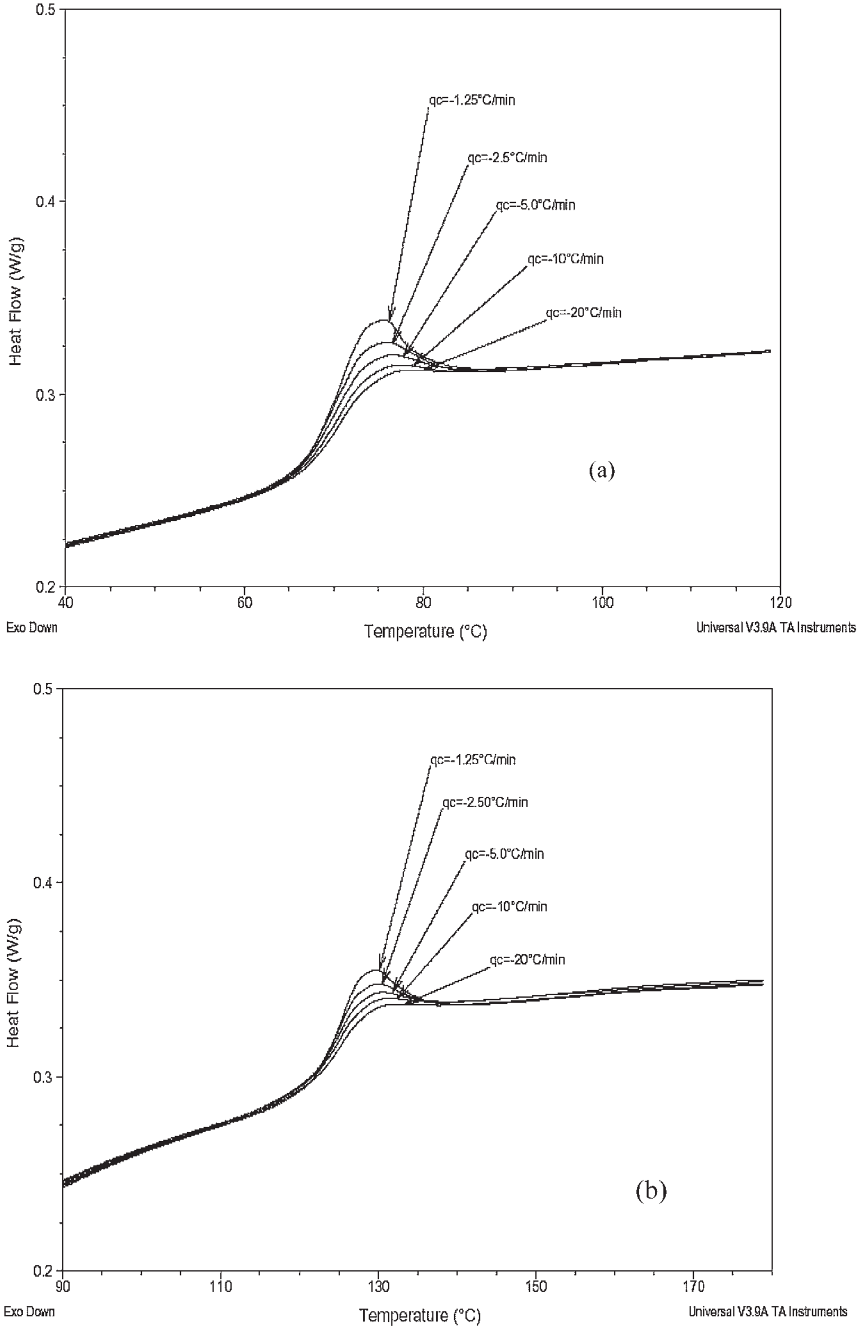

Figure 1.

Heating scans at 10 °C/min for PMMA1 (a) and PMMA5 (b) cooled at the rates indicated against each curve and immediately reheated in DSC. All the cooling and the heating scans concerning an experiment were run on the same sample.

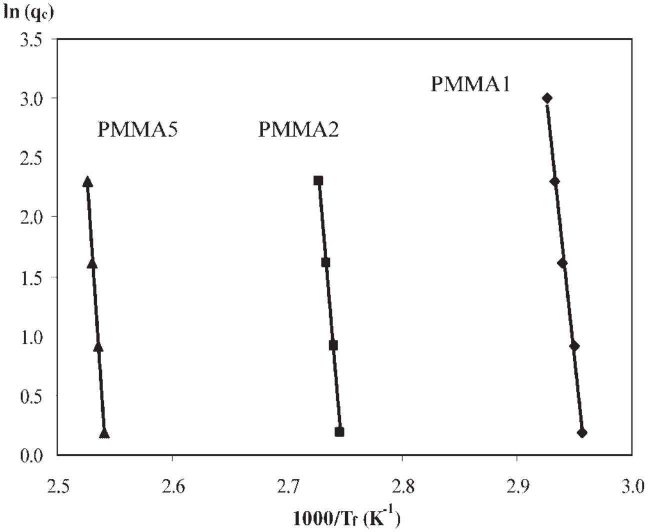

Figure 2.
Fictive temperature attained in the glassy state after cooling from equilibrium at different cooling rates q_c.

Table 2.
Δh^* evaluated from the different cooling rate experiments.

Sample	$\Delta h^*/R$ (kK)	R^2
PMMA1	92.7	0.992
PMMA2	115.8	0.997
PMMA3	140.3	0.987
PMMA4	147.1	0.988
PMMA5	149.1	0.997

considering the samples PMMA1 and PMMA2 $\Delta h^*/R$ exhibits the highest growth, compared to the molecular weight increment (1,000 Dalton only), because PMMA2 molecular weight is close to the s-PMMA entanglement mass.

A typical set of DSC traces for a three-step thermal cycles is shown in Figure 4.a: an enthalpy overshoot during the reheating scan is observed. From these curves, the peak endotherm temperature T_p

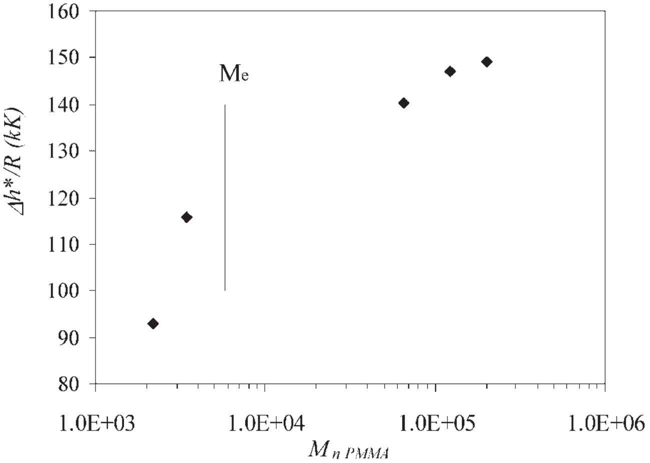

Figure 3.
Apparent activation energy determined from results shown in Figure 2 for the PMMA with varying molecular mass.

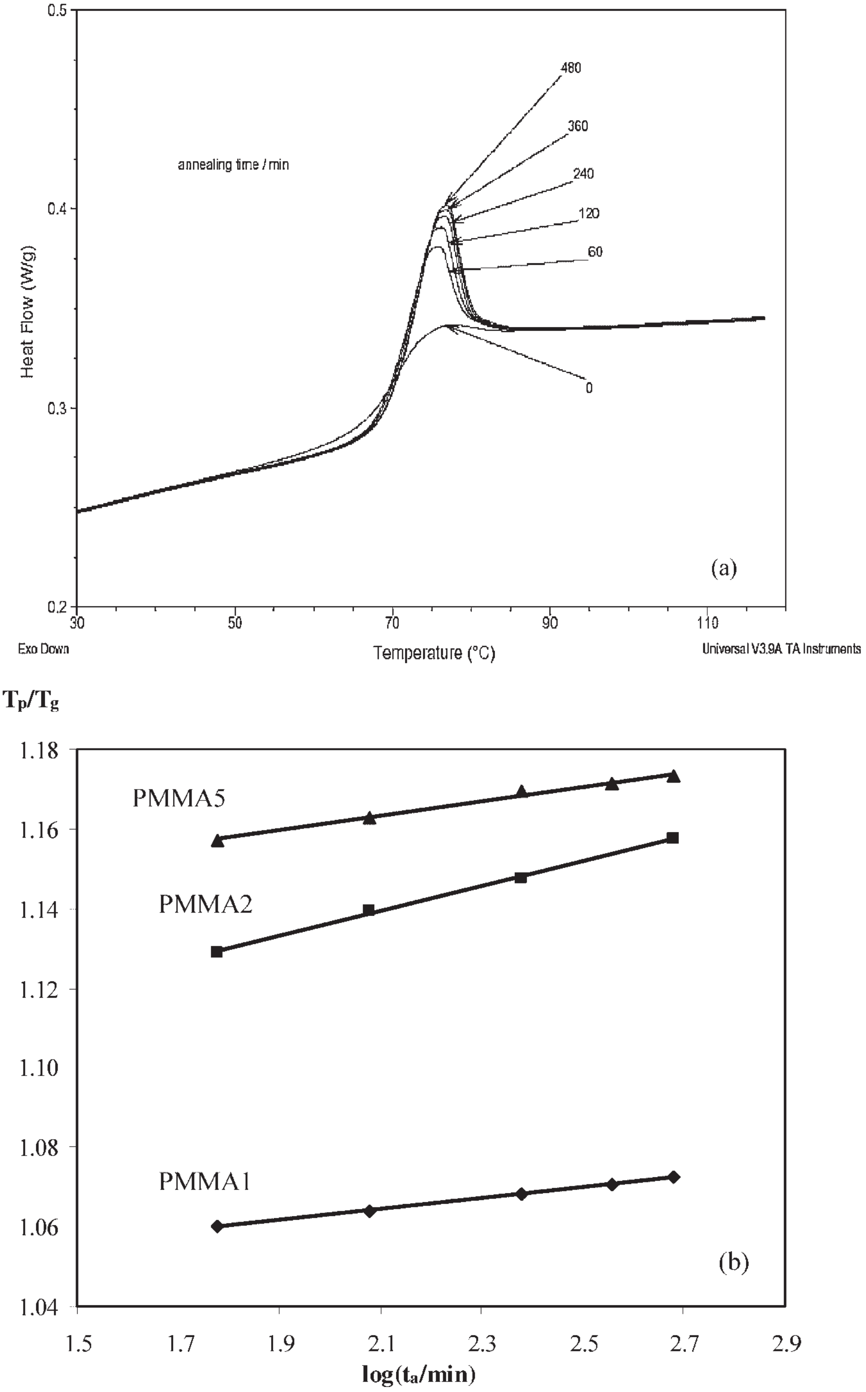

Figure 4.

a) DSC curves obtained in sample PMMA1 after annealing experiment at $T_g - 10\,^\circ$C for the times indicated; b) the dependence of normalized T_p respect to the annealing time for PMMA1, PMMA2 and PMMA5.

is obtained as a function of annealing time as reported in Figure 4.b: the usual behaviour of glassy polymer can be seen here with T_p increasing linearly with log (annealing time). The only deviation from this behaviour is for short annealing times for which the peak temperature appears to remain constant.[12]

As a general procedure in calorimetric experiments, the enthalpy lost on aging a glass for a period of time t_a at a given temperature T_a can be evaluated according to the relation (2):

$$\Delta H(T_a,t_a)=\int_{T_x}^{T_y}\{C_p^a(T)-C_p^u(T)\}\partial T \qquad (2)$$

where $C_p^a(T)$ and $C_p^u(T)$ are the heat capacity measured after the annealing and that of the unannealed sample, while T_x and T_y are the reference temperature ($T_x < T_g < T_y$) where the two signals overlap.[1] This procedures provides the experimentally enthalpy difference after two thermal treatments, with and without annealing.

In Figure 5.a a schematic behaviour of ΔH (T_a, t_a) as a function of log t_a is plotted and the relaxation rate and the plateau value which characterized the enthalpy relaxation process are shown. The relaxation rate R_H (T_a) of the enthalpic relaxation process is defined as the inflectional slope of

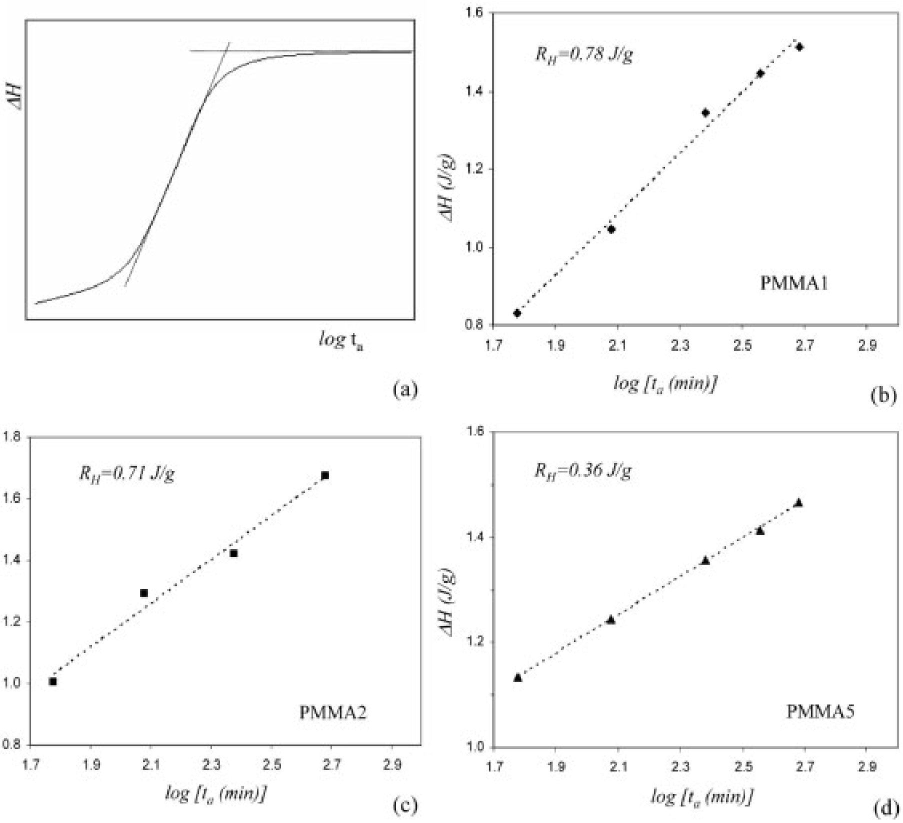

Figure 5.
(a) Schematic behaviour of the enthalpy lost on aging a glass as a function of annealing time; inflectional slope, defining the relaxation rate R_H, and the plateau value of ΔH are shown. (b)–(d) Enthalpy lost on annealing at $T_a = T_g - 10$ °C as a function of annealing time evaluated using equation (4) for PMMA1, PMMA2 and PMMA5 respectively; the values of the apparent relaxation rate are reported in the figures.

the relaxation isotherm[13]:

$$R_H(T_a) = \frac{d\Delta H(T_a, t_a)}{d \log t_a}\bigg|_{\text{inf}}. \tag{3}$$

This parameter turns out useful in comparing the relaxation kinetics of our glass forming systems, characterized by different molecular weights. In Figure 5.b, 5.c and 5.d the experimental results concerning ΔH (T_a, t_a) *vs log* t_a for three samples and the corresponding linear interpolation are reported.

As R_H is a function of time, for the time range explored we are not able to say if the annealing process stays within the "intermediate" range of overall sigmoidal behaviour or not; in fact in the case of PMMA1, Figure 5.b, it seems that the interpolation is of both the intermediate and the upper end of the sigmoidally shaped behaviour, giving an under-estimating value of R_H. For this reason the evaluated R_H (T_a) are discussed as apparent relaxation rate.

On going from PMMA1 to PMMA5, the apparent relaxation rate R_H (T_a) of the relaxation isotherm at $T_g - 10\,^\circ$C, decreases with a function which is non-linear with the respect to the increase of molecular weight.

As reported in literature for polystyrene samples[14] and for atactic PMMA,[15] the relaxation rates of enthalpy relaxation as a function of molecular weight evidenced a step like behaviour with the onset close to the entanglement mass. In our case we are near the onset of the step like behaviour with PMMA1 and PMMA2 samples, being the entanglement mass 5,800 Dalton for a syndiotactic PMMA, while the higher PMMA molecular weights are in the plateau region, as shown in Figure 6.

Conclusions

In this work a study carried out by means of DSC experiments on enthalpy relaxation of syndiotactic PMMA narrow fractions has been presented.

The apparent activation energy of the enthalpy relaxation process was evaluated for five s-PMMA with molecular masses ranging from 2,000 to 200,000 Dalton: a continuously increase with the molecular mass has been found. Interestingly, the highest growth compared to the molecular

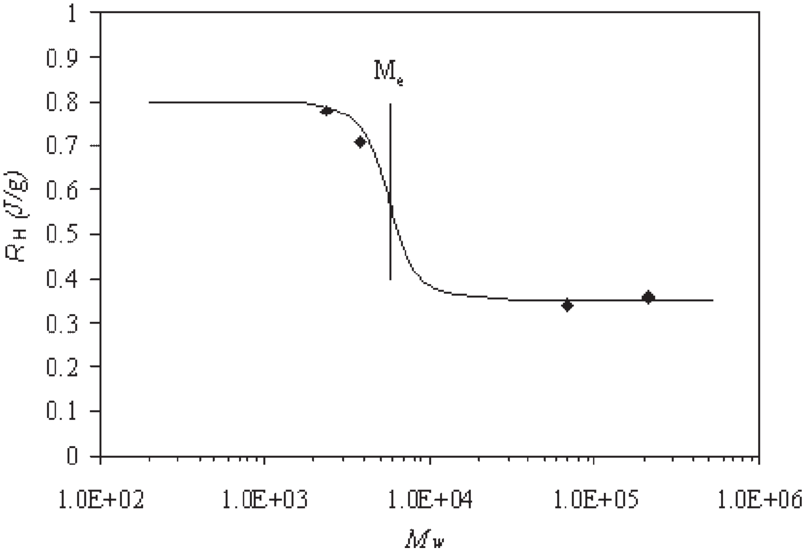

Figure 6.
Enthalpy apparent relaxation rate as a function of the molecular weight of s-PMMA at $T_g - 10\,^\circ$C. The line is a guide line.

weight increment was observed in the samples with molecular masses close to the s-PMMA entanglement molecular mass.

The effect of constraints arising in polymeric dynamics as the molecular mass increase was highlighted evaluating the enthalpy apparent relaxation rates. The chance in molecular mass of s-PMMA produces a change in the apparent relaxation rate which is strongly related to the molecular mass entanglement of the polymer.

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